ENAMELS

Robert D. Landrum

FOREWORD

This little book is a collection of the various articles on Enamel published by the writer in the various technical journals to which credit is given with each article.

There are also included some tables of interest to the Enameling industry and space is provided at the end of the volume for additional data of this kind.

The book is published for the benefit of the Enameling industry by THE HARSHAW FULLER & GOODWIN COMPANY, Cleveland, Ohio, and is presented with its compliments.

<div align="right">Robert D. Landrum</div>

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ENAMELS FOR SHEET STEEL *[1]

Enamels for sheet steel are boro-silicates of sodium, potassium, calcium and aluminum and are, in every sense of the word, glasses. Such enamels are so compounded that they form a homogeneous, glossy coating on the surface of the sheet steel utensil, which will not be corroded by the acids or alkalies used in cooking and which will resist punishment both by impact and by rapid changes of temperature.

Although an enamel is a glass, the fact that it must adhere to steel and resist the abuse common to cooking utensils makes necessary the addition of other ingredients besides those used in manufacturing ordinary glass. In enamels, ground quartz, flint or sand supply the silica, and feldspar and clay, the alumina. Fluorspar or calcite is added to supply the lime and cryolite to render the enamel translucent. Soda ash and pearl ash are fluxes adding sodium oxide or potassium oxide to the product, and borax furnishes the boric anhydride, which adds many desirable qualities, such as greater ductility and elasticity. Sodium or potassium nitrate is used in white enamels and manganese dioxide in dark colored enamels as an oxidizing agent. Oxide of cobalt is used in enamels which come directly in contact with the steel and adds adhesiveness to this coating.

For producing white enamels, oxide of tin is used; for blue, cobalt; for violet and brown, manganese; for gray, nickel; for green, copper or chromium; for yellow, uranium or titanium; and for red, iron, selenium or gold.

Enameling is still held as a secret art, and the formulas are carefully guarded. Most companies allow very few visitors to go through their plants and some keep their employees in ignorance by various schemes. In one American works, each of the enamel raw-materials is given a number. They are ordered, shipped, kept account of, and stored under their respective numbers, and only those in authority even know what materials are used. In this same factory, employees of one department are not allowed in another and after being employed in one department, a man is barred from employment in any other. Some works have the formula for each enamel divided into two parts, one of which is mixed by one man, the other by a second, and certain proportions of each are then mixed together by a third man. In practically all enameling works, the materials are weighed on a scale, the beam of which is hidden from the laborers, who are also generally of foreign birth and are changed frequently.

The "Black Shape."—The sheet steel which is used for enameled ware is as nearly as is possible free from carbon, silicon, sulphur and phosphorus, and its manganese content is generally about 0.2 per cent. These sheets come in squares and oblongs from 27 to 20 gauge and are circled, stamped and spun with as little heat treatment as possible and with the use of a lubricant that can easily be cleaned off. The ears, handles and other trimmings are, as far as is practical, welded on, as riveted joints are difficult to enamel.

Pickling Process.—The surfaces of the completed steel vessels are thoroughly freed from carbonaceous matter by annealing at a low red-heat and are then pickled in hot dilute acid, thoroughly rinsed in water, and then in weak alkali solution. After a quick drying they are ready to be enameled.

The Enamel.—In the making of an enamel, the various raw-materials are loaded from their respective bins

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into small cars called "dollies." These are filled to a line which approximates the correct weight, then they are pulled on a scale, the beam of which is hidden from the workman, and the enamel-master indicates whether the load is light or heavy, and the workmen correct this by shoveling on more or taking some off. When each of the "dollies" is corrected so that the required amount of material for a mix is in it, all are dumped on a large, hard maple floor, the coarser material on the bottom and the finer on the top. This pile is thoroughly mixed by shoveling, and is loaded into an electric elevator, which hoists it to its bin. There is a bin for each different kind of enamel, and a traveling bucket which holds a melt (about 1200 pounds) carries the mix to the tank furnaces where it is melted into a liquid glass.

These tank furnaces are regenerative, reverberatory furnaces like those used in the manufacture of glass, and natural gas or crude oil is an ideal fuel for them. However, in the older enameling works, coal is used directly, and in the later ones producer-gas is used as a fuel. The temperature required for smelting the different enamels varies from 1000° C. for a glaze to 1300° C. for a ground coat, and, in most enameling works, pyrometers are installed to assist in controlling these temperatures. Each furnace will give seven or eight melts in twenty-four hours.

After the enamel is melted into a liquid glass, a fire-clay plug in the front of the furnace is pulled out and the glowing liquid stream plunges out and is caught in a tank of cold running water. The reaction is terrific and the glass mass is torn and shredded, cracking into small pieces like popcorn, each of which is a myriad of microscopic seams and fissures. This "quenching," as the process is called, toughens the enamel and facilitates the process of grinding which comes next.

The water is drained from the tanks, leaving the "enamel frit." This is shoveled into pans (a certain weight to a pan) and is ready for grinding.

In the mill room, the enamel frit is ground in large ball mills for about thirty hours. These mills are cylindrical, about five feet long and six feet in diameter, and are lined with porcelain bricks. The frit is put into them with fifty per cent. of water and several per cent. of white ball-clay. For the white cover-coat enamels, tin oxide is also added. The mill revolves and the constant impact of the flint stones against the glass particles grinds them to an impalpable powder, which mixes with the water and the clay, forming a mass which has the consistency of rich cream. This is loaded into tanks, where it is allowed to age a week or so.

Application of the Enamel.—From the mill room the enamel is taken to the dipping room, where it is put into tanks that are like large dish-pans. These are sunk into tables, and at each tank a slusher works. The slusher takes the stamped-out steel vessel, which has been thoroughly cleaned, and plunges it into the enamel. When taken out, the wet enamel forms a thin film over the entire surface. By a gentle swinging motion, the excess of enamel is thrown off, and the vessel is placed bottom down on three metal points projecting from a board. Three or four vessels are put on a board; these are placed on racks and when the vessels are thoroughly dry they are carried to the furnace room.

The furnace room contains a long bank of muffle-furnaces and in these the ware is put after drying. The temperature in these furnaces is about 1000° C. and here the little powdered particles of enamel are fused together in a solid glass coating over the vessel, the process requiring from three to five minutes.

Each coat is burned separately. For instance, we have a pudding pan that is to be a three-coat white inside, turquoise-blue mottle outside. It is first dipped in the ground coat enamel, the excess is shaken off and the vessel put on a three-pointed rack and dried. After drying, the enamel stands in little grains all over the surface

of the ware, adhering to the metal on account of the raw clay ground with it. At this stage every care must be taken, for a scraping, even of the finger nail, would take off some of the powdered particles of the enamel. This pan is then put into the muffle of the furnace, and the heat fuses all the little particles together, leaving a tight-holding vitreous coating all over the surface of the vessel. This fundamental coating is nearly black, due to the oxides of cobalt and nickel which it contains, and shines with a glass-like luster.

After the vessel has cooled at the ordinary temperature of the room, it is again brought to the slushing room, and here is covered with an enamel—this time a white. It goes through the same process as before, except that a black bead is brushed around the rim. On account of the dark color of the first coat showing through, this second coat, after it is burned, has a gray appearance, and is called the "gray coat" or "first white." The vessel is again sent to the slushing room, and is dipped into a white enamel, the excess shaken off, and before drying the blue-green enamel is sprayed on the outside.

This spraying process was at one time done by dipping a wire brush into the wet blue-green enamel and the slusher shaking it over the surface of the vessel, causing the blue enamel to fall in little speckles all over the white enamel. In most factories, however, spraying machines, which work on the principle of an atomizer, have been installed. A tank full of the colored enamel stands over the table and the enamel is forced out through a nozzle in a spray by compressed air. The flowing of the enamel is controlled by the foot of the slusher as he holds the vessel in the spray. The vessel is then dried and the coating is fused in the muffle-furnace, the result being turquoise-blue spots on a white background.

The finished ware is assorted into three lots: firsts, seconds, and job lots. Some of the seconds and job lots

are fit for redipping. They may have some little spots where the original vessel was not properly cleaned and where, on account of the rust or dirt, the enamel did not adhere. These spots are filed or are held under a sandblast until the exposed surface is perfectly clean, and then the vessel is covered with another coat of enamel.

There are schemes for saving money in all manufacturing plants, and in the enameling business a large part of the profit comes from the residues. For instance, every bit of enamel is scraped from the tanks and tables, all sweepings from floors are saved, and all the waste water from the various departments is first carried into catch basins, and every few days these are cleaned and the residue, which has settled to the bottom, is taken out. The residues from all these sources are again melted with the proper amount of fluxing material and coloring matter, and this dark-colored enamel is used for coating the cheaper wares.

A German White Enamel.—In order to give an idea of the composition of a white cover-coat frit, such as is used on cooking utensils, and to show the method used by ceramists to calculate its so-called molecular formula, the following enamel, the formula of which is taken from the 1911[1] edition of the "Taschenbuch für Keramiker," is used:

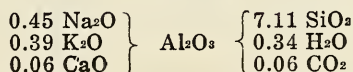Feldspar 38.6 per cent., quartz 19.0 per cent., borax 15.4 per cent., cryolite 11.7 per cent., saltpeter 6.5 per cent., calcite 6.5 per cent., fluorspar 1.3 per cent. and magnesium carbonate 1.0 per cent.

Enamel Materials.—All the materials used were practically pure except the feldspar, which was a pegmatite of the following composition:

[1] Page 18. Published by Keramische Rundschau, Berlin, N. W., 21.

		Per cent.
Silica	(SiO_2)	70.66
Alumina	Al_2O_3	16.85
Potassium oxide	K_2O	5.93
Sodium oxide	Na_2O	4.61
Lime	CaO	0.52
Carbon dioxide	CO_2	0.41
Moisture	H_2O	1.02

This figures to a "molecular" formula of

$$\left. \begin{array}{l} 0.45\ Na_2O \\ 0.39\ K_2O \\ 0.06\ CaO \end{array} \right\} \quad Al_2O_3 \quad \left\{ \begin{array}{l} 7.11\ SiO_2 \\ 0.34\ H_2O \\ 0.06\ CO_2 \end{array} \right.$$
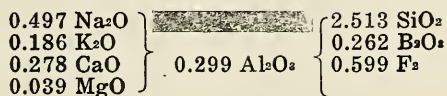
the molecular weight of which would be 602.

The other materials used were:

Material	Formula	Equivalent weight
Quartz	SiO_2	60
Borax	$Na_2O \cdot 2B_2O_3 \cdot 10H_2O$	382
Cryolite	$2Na_3AlF_6$, giving $3Na_2O \cdot Al_2O_3 \cdot 6F_2$ ...	420
Saltpeter	$2K_2O \cdot N_2O_5$	202
Calcite	$CaO \cdot CO_2$	100
Fluorspar	CaF_2, giving $CaO \cdot F_2$	78
Magnesium carbonate	$MgO \cdot CO_2$	84
Feldspar	(Given above)	602

The above total corresponds to the following molecular formula of enamel:

$$\left. \begin{array}{l} 0.497\ Na_2O \\ 0.186\ K_2O \\ 0.278\ CaO \\ 0.039\ MgO \end{array} \right\} \quad 0.299\ Al_2O_3 \quad \left\{ \begin{array}{l} 2.513\ SiO_2 \\ 0.262\ B_2O_3 \\ 0.599\ F_2 \end{array} \right.$$

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THE ENAMEL[1]

Batch Mix — Material	Per cent. used	M. W.	Molecular equivalent[2]	Na₂O	K₂O	CaO	MgO	Al₂O₃	SiO₂	B₂O₃	F₃
Feldspar	38.6	602	0.0641	0.0288	0.0250	0.0038	..	0.0641	0.4558	..	..
Quartz	19.0	60	0.3167	..	..		..	..	0.3167	..	..
Borax	15.4	382	0.0403	0.0403	..	..	..	..		0.0806	..
Cryolite	11.7	420	0.0279	0.0837	..	..	..	0.0279	..	..	0.1674
Saltpeter	6.5	202	0.0322	..	0.0322	..	..	..	..	..	..
Calcite	6.5	100	0.0650			0.0650	..	..	..	..	..
Fluorspar	1.3	78	0.0167			0.0167	..	..	..	..	0.0167
Magnesium carbonate	1.0	84	0.0119			..	0.0119	..	..	..	..
Total	..	..	..	0.1528	0.0572	0.0855	0.0119	0.0920	0.7725	0.0806	0.1841

[1] Complete data in regard to this enamel is given on page ——.
[2] Molecular equivalent equals per cent. used divided by M. W.

THE FUNCTION OF THE VARIOUS RAW MATERIALS
IN A SHEET STEEL ENAMEL*

An enamel, such as is used on cooking utensils, is a glass of such nature that it will adhere to steel and on account of this, its composition is more complicated than that of ordinary glass. The materials used to make ordinary glass are sand, limestone and soda ash, with lead oxide added to certain types. These glasses, however, will not adhere to iron and have a co-efficient of expansion entirely different from that of sheet steel, and also the temperature at which they must be melted would soften the steel shape. An enamel, then, although a glass in every sense of the word, and containing the elements introduced by these glass materials, also contains others added to modify the physical properties and to suit it for the purpose intended.

Quartz and Flint

Sand is the material which furnishes silica (SiO_2) to glass and it is sometimes used in enamels. However, enamels must melt at a much lower temperature than glass and thus require the silica-furnishing material to be very finely powdered in order that it may combine with the other materials at this lower temperature. As it is more expensive to pulverize sand than it is to pulverize quartz or flint, one of these minerals—each having the same chemical composition as sand—is generally used.

It may be taken as a general rule that other things remaining constant, the higher the per cent of silica the higher will be the melting point of the enamel and the

greater its acid resistance. Silica also has a low co-efficient of expansion and increasing it in an enamel lowers the co-efficient of expansion of that enamel. Therefore, one method of regulating an enamel coating is to **increase** the silica when the enamel is inclined to split off when cooling after muffle burning. This remedy is indicated when the curve of the enamel chips, showing that the enamel contracts less rapidly on cooling than the iron.

Soda Ash

In glass, all of the sodium oxide is introduced as soda ash, while in enamel, this material is only used when it is desirable to add the sodium oxide without the introduction of any other ingredient.

Up to a certain point the addition of silica to an enamel formula may lower the melting point. An exaggerated example is that Calcium Oxide (lime) alone is practically infusible, but on adding silica, a fairly easily fusible glass is formed.

Soda Ash is commercially pure anhydrous sodium carbonate (Na_2CO_3) and, therefore, besides adding the sodium oxide to the finished enamel, gives off carbon-dioxide gas during smelting and the melted mass is then quite thoroughly stirred by the evolution of this gas and many impurities are carried off.

The function of the sodium oxide is to combine with the other materials (especially the silica) and form a vitreous product. The larger the proportion of sodium oxide (in comparison with the amount of silica present) the lower will be the melting point of the product and the less resistant to acids it will be. At the same time, however, an increase of the sodium oxide tends to make the product more flexible and less brittle.

Many enamels do not include soda ash in their batch mix formulas as sufficient sodium oxide is furnished by the feldspar, cryolite and borax.

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Fluorspar and Calcite

Fluorspar and Calcite are the minerals which are used to supply the lime (CaO) to enamels. In glass, limestone furnishes this important ingredient, but on account of the impurities, always present in this mineral, it cannot be used in the more carefully compounded enamels. Both Fluorspar and Calcite have their advantages and disadvantages and, as their cost is about the same, a careful consideration of these is necessary before one can decide which is the better to use in an enamel. American practice is inclined to favor the use of Fluorspar.

Fluorspar

The calcium present in Fluorspar seems to combine more easily with the other ingredients of the enamel batch than does the calcium oxide of calcite. This is evident from the fact that Fluorspar enamels melt at a lower temperature and become homogeneous in a shorter time than calcite enamels. In enamels, which derive some of their opacity from cryolite, this is of particular advantage, for it is a well known fact that the longer a cryolite enamel is smelted, the less opaque it becomes.

The disadvantages pertinent to the use of fluorspar instead of calcite in an enamel formula are due to two things; this mineral contains fluorine and is a powerful reducing agent at the temperature attained in the smelter. The fluorine is set free during the smelting and, although the virtues of fluorspar are very likely due to the energetic action of this element, it is also active in corroding the furnace linings and the life of the smelter is shortened.

The reducing action of this mineral makes it very necessary to carefully regulate the smelter so that the atmosphere is always oxidizing and where a large amount is used the percentage of nitrate in the batch mix must be increased.

Calcite

Calcite in enamels does not act as a reducing agent nor does the gas given off by it (CO_2) attack the furnace linings. Therefore, the life of the smelter is longer and there is no necessity for adding more nitrate nor of so carefully controlling the atmosphere of the smelter.

The disadvantages common to a calcite enamel are due to its requiring a higher temperature and a longer time to combine with the other ingredients of the batch. With cryolite enamels, this longer smelting is certain to cause them to lose some of their opacity.

Defects Caused by Fluorspar and Calcite

Unless sufficiently smelted and thoroughly oxidized, fluorspar enamels are not stable and, on standing, lose their gloss, while calcite enamels, unless smelted entirely homogeneous and free from carbonate, are inclined to chip and scale and to form bubbles and blowholes where the enamel is applied thickest.

Calcium Oxide (CaO)

The calcium oxide introduced by either of these materials will replace sodium oxide in an enamel formula and, while not affecting the melting point to any great extent, makes the enamel much harder, more acid resistant, more glossy and more opaque. Calcium oxide increases the brittleness of an enamel, however, but at the same time it allows the addition of more boric anhydrid and this ingredient counteracts this effect.

Feldspar

Feldspar is generally included in the batch mix of any enamel. The new element introduced by this material is aluminum in the form of alumina (Al_2O_3). It also adds sodium oxide (Na_2O) or potassium oxide (K_2O) or both and at a much cheaper price per pound than they can be bought in any other form.

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The other ingredient introduced by feldspar is silica (SiO_2) and it is likely that **its** introduction **thus** has the advantage over its introduction as quartz or flint, in that, in feldspar, nature has already combined the alumina and the silica. An enamel, therefore, getting its silica from feldspar requires less heat in smelting than one getting the silica otherwise.

The alumina added by the feldspar makes the glass softer and also less resistant to acids, but when other suitable ingredients are present, causes the enamel to become translucent. It also lessens the tendency of the enamel to chip but makes it more liable to craze. It combines directly with the other ingredients forming a homogeneous product and, therefore, does not aid in improving the stretching qualities of the product as does the alumina added as clay, which material will be taken up later.

Borax and Boric Acid

One of the most characteristic ingredients of an enamel is boric anhydrid (B_2O_3) and this is furnished to the batch mix by borax or boric acid.

Borax is generally used for this purpose, as it is much cheaper and the only enamel in which its use is prohibited are those whose full quota of sodium oxide is furnished by the feldspar and cryolite. Borax contains 16% of sodium oxide, so in such enamels, boric acid ($B_2O_3.3H_2O$) would be used.

Boric anhydrid (B_2O_3) makes the enamel more elastic, less brittle and changes the co-efficient of expansion in such a way that the glass produced may be used on steel. It is like the silica in many ways, increasing the acid resistance and allowing more alkalies and metal and earth oxides to be used in the mix and like silica causes the enamel to chip when present in excess.

Unlike silica, however, it increases the viscosity of the smelted enamel and lengthens the period between the temperature at which the enamel will melt to form a

homogeneous vitreous coating and the temperature at which it will "burn off," thus making the enamel less liable to be spoiled by poor shop practice.

This property of viscosity, which the boric anhydrid increases, causes the enamel to remain thick and gummy on the black shape, while being heated in the muffle, instead of getting thin and running off as would ordinary glass.

Clay

Clay is always used in the mill mix of an enamel that is to be slushed on wet and is sometimes included in the ingredients that go into the smelter. In the latter case, it is used to introduce alumina and silica, as does feldspar, but without introducing any alkalies. Clay is quite infusible and very finely divided, thus adding opacity to the enamel. When added at the mill, it gives besides the qualities already mentioned plasticity to the wet enamel and holds up the glass particles during slushing. It also causes the powdered glass particles to adhere to the steel shape during the drying before muffle burning.

Whether added at the mill or in the smelter, clay adds to the stretching qualities of the finished enamel coating. This is accounted for by the infusibility of the clay, with property keeps it from entering into complete combination with the other materials. Instead, it holds the glass masses (with which each particle of clay is surrounded) apart during the contraction of the steel and allows them to pull away from it without chipping during expansion. Under the microscope, enamels with a high clay content are very porous—the higher the clay the more porous—and, therefore, clay in an enamel always lessens the gloss. This is the prime factor in limiting the amount of clay that can be used in an enamel.

Stellmittle

The plasticity of clays in water can be greatly increased by adding to the water very small quantities of acids, bases or salts which dissociate in the water. These

cause the clay to assume a colloidal form quite jelly-like in nature and thus make the enamel batch in which they are present much thicker without removing any of the water.

These are called "Stellmittle" or fixation materials by the German enamelers. Any acid will answer, but, as the effect on the finished product is deleterious, these are seldom used. **Borax** (a saturated solution in hot water) or a mixture of this with a saturated solution of sodium carbonate is generally used in ground coat enamels and may be used in small quantities in white enamels. **Magnesium Sulfate** has much favor with most enamelers and its principal virtue is that less of it is required than of any of the others. Magnesium sulfate cannot be used in the ground coat, as it will cause the iron to rust.

Magnesium Oxide and Carbonate are used in the mill mix and are good for this purpose, as also is ammonium chloride, ammonium carbonate and ammonium acetate. Some enamelers also use the sulfate of sodium but any of the sulfates will impair the gloss of the product.

Oxide of Tin

Tin oxide is one of the most important and, at the same time, most expensive of the enameling materials. Indeed a French writer defines an enamel as "an opaque glaze containing tin oxide."

Added to the smelting batch, up to about 3% of the stannic oxide—the commercial oxide of tin—is reduced to stanous oxide, which forms a transparent compound with the silica. All over 3%, and practically all added at the mill, remains in suspension in the enamel, and, keeping its intense white color, makes the enamel opaque.

The writer has used as high as 30% of this material in an excellent, though costly, enamel, but the amount used in white enamels for cooking utensils seldom runs below 5% or above 15% in the finished product.

All efforts to entirely replace this material with a cheaper one have led to the conclusion that some oxide of tin is absolutely necessary in a white enamel. Other materials can replace part of it, but the question as to whether there is any actual saving in so doing is a matter of dispute.

The higher the percentage of tin oxide in an enamel the thinner it may be applied and attain a given standard of whiteness. This thin application reduces the production cost in two ways, viz., less enamel is required and the number of seconds, caused by the scaling off of the too thick coatings, will be greatly reduced. But of still more importance is the fact that the thin application of the enamel adds greatly to the durability of the ware under punishment both by impact and by sudden changes of temperature, thus adding to the reputation of the manufacturer. Then too, the opacity produced by this material is practically "fool proof." The tin oxide substitutes must be handled with the greatest of care during every operation and the slightest variation of method of procedure is likely to spoil the enamel.

Cryolite

The only material which produces opacity besides the tin oxide and which has stood the test of time is cryolite. This material must be added in the smelter and although it adds no new elements those added are so geologically combined that at a certain temperature they make the enamel frit quite translucent and even opaque when thickly applied. The amount of this material which can be used in a given enamel is limited by the large amount of sodium oxide which it introduces. Cryolite is a double fluoride of aluminum and sodium and in the enamel about 20% of its mass escapes as fluorine gas and is replaced by oxygen. Thus it is very necessary to keep the atmosphere of the smelter oxidizing, and this is best done by having sufficient nitrate present in the enamel batch. The opacity produced by cryolite is quite elusive

and the greatest care must be taken to have the temperature, both of the smelter and the muffle furnace, right and the length of time for smelting and burning correct.

Oxide of Antimony

Antimony Oxide is another substitute for tin oxide and like cryolite this is added in the smelter. Antimony-containing enamels are quite opaque, if applied in thick layers; thin coats of such enamels, however, are quite transparent and it is doubtful whether or not antimony has any great coloring effect on a properly applied enamel. Antimony oxide is in itself quite poisonous and when used in quantities large enough to give the desired opacity, there is a danger that some of it may be made soluble in the cooking acids and thus be detrimental to the health of the consumer. In practice most antimony enamels contain less than 5% of this material.

Both antimony and tin oxide and, in fact, all metallic oxides add lustre to the enamel coating, for they increase the density and it has been shown that the gloss of a glass or enamel increases directly with the density.

Zinc Oxide

The oxide of zinc is the only metallic oxide, except that of tin, which can be safely added to a white enamel for the purpose of increasing its luster, and even it will lower the resistance to corrosion by acids of such an enamel very markedly.

Used in large quantities and in very soft enamels it produces some opacity. Its main use, however, is as a substitute for the objectionable lead oxide in formulas for colored enamels. Like lead, it has the property of making such colors more brilliant.

Saltpeter and Chili Saltpeter

Potassium nitrate (saltpeter) or sodium nitrate (Chili Saltpeter) is used in enamels, which require oxidizing agents in the smelter.

Oxidizing agents are necessary in enamel formulas which contain fluorspar or cryolite to replace the fluorine given off in the smelter and also in white enamels containing iron as an impurity. In the latter case, they change all of the iron to the higher oxide which has a less intense coloring action on the enamel.

Sodium nitrate is much cheaper than potassium nitrate but must be stored in air tight containers as it is very deliquescent. The impracticability of storing the material has forced manufacturers to use the more expensive nitrate or to employ a chemist to make daily determinations of its moisture content. Then too, experiment has shown that the presence of potash in an enamel already containing soda tends to increase the gloss and to lower the melting point without affecting the other properties. This would be a reason for using nitrate of potash instead of nitrate of soda in an enamel, in which potash is not supplied by some other material, for potassium oxide remains from the saltpeter, while sodium oxide remains from the Chili saltpeter.

Manganese Di-Oxide

Manganese di-oxide (MnO_2) is a strong oxidizing agent and its use in enamels is primarily due to this fact. Used in an enamel batch, it disintegrates during smelting into manganous oxide (MnO) and oxygen gas and the latter, besides stirring the molten enamel, changes some of the ingredients to their highest possible oxides.

This action is especially desirable in ground coats which must stand a hot fire in the muffle, as it renders over-burning during this operation less probable.

Manganese compounds cannot be used in white enamels in more than minute quantities as it colors the glaze an amethyst purple. Its second use in enamels is due to this coloring action and it is used in many colored enamels.
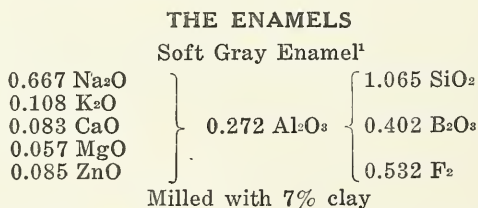
Oxide of Cobalt

Oxide of Cobalt (CO_3O_4) is added to enamels either to give them a blue color or to make them adhere directly to the steel. For the second reason, all successful ground coats contain oxide of cobalt. An enamel may be so compounded that its co-efficient of expansion will be exactly that of the sheet steel upon which it is to be used, and, yet without the addition of oxide of cobalt, according to the writer's experience, it cannot be made to adhere to the steel as well as with this addition. There are many theories as to the exact function of cobalt in a ground coat enamel and the popular one at present, is that silicate of cobalt in the enamel frit is reduced during muffle burning to a lower silicate and perhaps to metallic cobalt. The oxygen, which is given off in either case then unites with the iron of the black shape and is taken into the enamel as ferrous silicate and, if metallic cobalt is left, this unites with the iron of the black shape, forming a widely distributed porous alloy. At any rate, there is an interaction between the cobalt of the enamel and the iron of the black shape which binds the enamel to the steel. Whether this is the correct explanation of the action, we do not know, but it is certain from practical experience that the cobalt-containing ground coat enamels are more easily burned correctly by the men in charge of the muffle furnaces. This is explained by the fact that there is a definite, though delicate, color change from blue to green in cobalt-containing ground coat enamels at just the point at which the enamel so fired will adhere most firmly to the steel coat. Such an enamel, when correctly burned, will have a very characteristic greenish tinge; when under-burned a blue color, and, when over-burned, a brownish black color.

RESISTANCE OF SHEET STEEL ENAMELS TO SOLUTION BY ACETIC ACIDS OF VARIOUS STRENGTHS*

Certain enameled wares have been advertised as capable of withstanding 80 per cent. or 90 per cent. acetic acid solutions, and although this was found to be a true statement still it was misleading, for these very wares were unable to resist the action of ordinary vinegar which contained but 5 per cent. acetic acid. This phenomenon is explained by the chemist as being due to the fact that a 5 per cent. solution of acetic acid is very much more dissociated than one of 80 or 90 per cent. and therefore its dissolving action (which is directly proportional to its dissociation) is much the greater.

To show the action of various mixtures of this common cooking acid and water, the two series of tests were made upon enamels typical of some of the cheap wares on the market.

The First Series of experiments was made upon a gray enamel, mottled with dark brown. As the dark enamel was made up from residues, and as the proportions of the two enamels on the dishes is uncertain, the exact molecular formula of the finished enamel coating cannot be given, but the formulas as calculated from the batch mix of the gray enamel and the analysis of the dark enamel frit (before milling) is given below.

THE ENAMELS

Soft Gray Enamel[1]

$$
\begin{array}{c}
\left.\begin{array}{l}
0.667\ Na_2O \\
0.108\ K_2O \\
0.083\ CaO \\
0.057\ MgO \\
0.085\ ZnO
\end{array}\right\}
\quad 0.272\ Al_2O_3
\left\{\begin{array}{l}
1.065\ SiO_2 \\
0.402\ B_2O_3 \\
0.532\ F_2
\end{array}\right.
\end{array}
$$

Milled with 7% clay

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*Reprinted from Transactions of American Ceramic Society. Vol. XIII, page 494.

[1] So called, as it is translucent instead of opaque and when milled without tin oxide—as was the case above—the dark ground coat shows through giving a gray effect.

Soft Dark Enamel for Spray

0.430 Na$_2$O				1.700 SiO$_2$
0.083 K$_2$O				
0.200 CaO				
0.045 MgO		0.114 Al$_2$O$_3$		0.430 B$_2$O$_3$
0.056 CuO				
0.010 CoO				
0.176 MnO				0.178 F$_2$

Milled with 7% clay

The Test

Nineteen miniature wash-basins about 8.5 centimeters in diameter and 2 centimeters in depth were slushed and burned in a dark colored ground coat, and then dipped into the gray enamel slush and when the excess was shaken off a light spray of the dark-colored enamel was flipped in with a brush. After drying they were burned at about Seger cone 09 in a muffle furnace. They were cooled in a desiccator and weighed accurately to one-tenth of a milligram (0.0001 gram). Into one of them was accurately measured (from two burettes graduated to 1/10 of a cubic centimeter) 0.25 cubic centimeter acetic acid[1] and 24.75 cubic centimeters distilled water, making a 1 per cent. solution by volume. Into a second dish was measured (as before) sufficient acid and water to make a 2 per cent. solution. Into a third a 3 per cent. and so on as given in the table following. These basins were then placed upon a gas hot-plate and evaporated to dryness without allowing them to boil vigorously.

When baked dry (fifteen minutes after apparent dryness) the dissolved residue was washed out at the tap, the dishes were scrubbed with a finger covered with a rubber finger-stall, rinsed thoroughly with distilled water, placed upon the hot-plate again until dry, cooled in a desiccator and again weighed. The loss in weight, which is equal to the amount of enamel dissolved in each case, is given below in milligrams.

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[1] This acetic acid was the ordinary c. p. 99% (1.05 sp. gr.) and by analysis contained 98.99% acid by weight.

Per cent acid	Enamel dissolved Mg	Per cent acid	Enamel dissolved Mg
1	4.8	25	17.9
2	6.9	30	18.9
3	10.1	40	13.0
4	12.1	50	8.9
5	14.9	60	5.0
7	16.9	70	3.1
9	18.5	80	1.6
15	21.3	90	0.3
17	22.0	100	0.0
20	22.4		

The Second Series was undertaken upon an enamel, the definite molecular formula of which can not be given.

The Enamel used was "soft gray enamel," the molecular formula of which is given above.

The Test used was the same as with the first series except that the miniature wash-basins were slushed and burned in three coats, viz., a dark ground, a good opaque white, and the "soft gray enamel" given above which was the top coat. These dishes are on exhibition and the results are given in the following table.

The Results

Per cent acetic acid	Enamel dissolved Mg	Per cent acetic acid	Enamel dissolved Mg
1	3.4	21	14.0
2	5.7	23	12.0
3	7.0	25	9.9
4	9.3	30	11.3
5	11.5	40	10.3
7	15.1	50	7.9
9	15.9	60	4.6
11	16.3	70	2.8
13	16.6	80	1.4
15	16.7	90	0.2
17	16.3	100	0.0
19	14.7		

The Enamel Solubility Curves

The accompanying sketch shows graphically the results of these two series of experiments. The various percentages of acetic acid solutions are laid off horizontally and the lengths of the vertical lines are proportional to the amount of enamel dissolved by the corresponding acid, one centimeter length of vertical line being equal to one milligram of dissolved enamel. The results of the first series, i. e., the one using the mottled enamel, are marked "X," while those of the second series, i. e., of the solid-colored enamel are marked "o."

N. B. The dip of the two curves from 21 per cent. to 30 per cent. acid is unexplained. Several independent trials at those points tended towards proving that this dip is not due to experimental error.

Discussion

MR. STALEY: This paper is interesting and instructive. As a practical method of testing the relative solubility of enamels in acid solutions, the method described has the commendable feature of being easily and rapidly performed. In point of accuracy, it is capable of being materially improved.

The shape of the solubility curve derived is very interesting. That the solubility should decrease as the acid becomes very concentrated is in accord with common experience.[1] But why should the solubility be greatest at 15 to 20 per cent. acid? Dissociation can hardly be at a maximum at this high concentration. Nor are we willing to grant that the solvent action of acetic acid is directly proportional to its dissociation. If we leave out of consideration the possibility that the acid solution may act toward the enamel simply as a solvent, dissolving it as water dissolves sugar, and treat the phenomena as a case of chemical attack by an acid, we must keep in mind the following considerations:

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[1] Foerster, "Action of Acids on Glass," Zeitschrf. Instraum., XIII, 457.

ENAMEL SOLUBILITY CURVES

Points marked X are the results of Series One,
those marked o Series Two.
Figures give results in millegrams

Trans. Am. Cer. Soc. Vol. XIII   Landrum
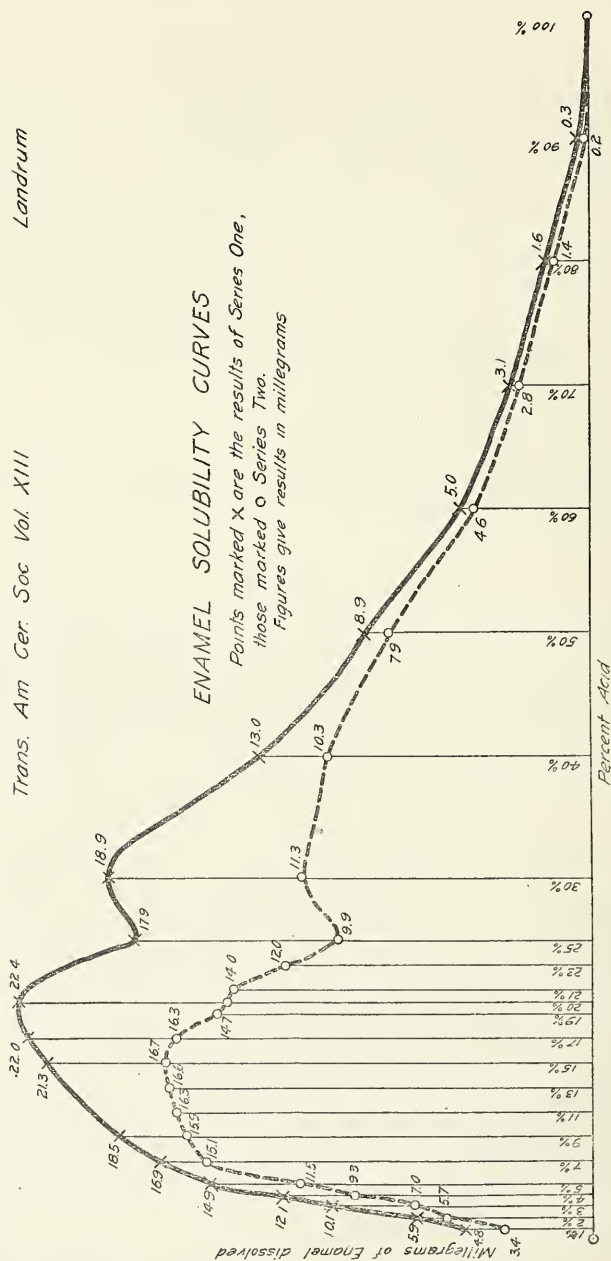
1. In dilute acid solutions, the acid is more dissociated than in concentrated solutions. This of itself means simply that we will have **more action in a given time per unit of acid** and does not mean that the more highly ionized acid is capable of dissolving more enamel if the reactions are allowed to come to equilibrium.

2. Dilute acid solutions **contain fewer units of acid.**

3. Very highly concentrated acid solutions have little action.

4. The concentration of the acid solutions varied continuously as they were boiled, becoming more and more concentrated as the boiling progressed. Therefore, the more dilute the acid the longer the time in which active concentrations would be operating. It also follows from this that the slower the rate at which the acid is concentrated, the greater will be its solvent action.

In accordance with these conflicting tendencies, we find the acid solutions of maximum solvent action are those of medium concentrations.

Acetic acid is one of the few organic acids that does not form a mixture of constant boiling point with water. The pure acid boils at 118° C. and in water solutions the water will start to come off at 100°C., and will come off the more rapidly the higher the temperature. So, if we should start with a given volume of what would be in this method approximately a 5 per cent. solution by volume of acetic acid and place it on a hot gas plate, we would soon have a smaller volume of 10 per cent., then 20 per cent. and so on up to a very small volume of 100 per cent. acid. The resulting solvent action would probably vary materially from what would be obtained by a treatment for a given time with an acetic acid solution of 5 per cent. strength. The latter results which would truly correspond to the title of the paper under discussion could be obtained by the use of a return condenser.

In order to determine the effect of the rate of evaporation on the solvent action of an acid solution of given strength, the following tests were made by the writer. Four pans coated with the same enamel were treated according to this method, the only variation in their treatment being that two pans were placed on a hot portion and two on a cooler portion of the same gas hot-plate. Violent boiling did not occur in either case.

The results are tabulated below:

No. of sample	Per cent of acetic acid	Time for evaporation in minutes	Enamel dissolved Mg
1	15	65	20.9
2	15	65	19.1
3	15	155	37.8
4	15	155	39.0

It would seem that in a test of this kind a constant temperature bath should be employed.

MR. LANDRUM: I agree with Mr. Staley that my title is rather misleading and might infer that this paper is intended as a research in pure chemistry instead of being merely a statement of the results of a series of practical tests made to demonstrate in a quick and convincing way the fact that an enameled ware may withstand the action of boiling 90 per cent. acid and still be attacked by acid solutions even as dilute as those used in cooking.

In these tests the conditions were very carefully kept as uniform as possible, and I might add that acetic acid and the method of boiling to dryness were used simply because I was trying to duplicate the method used on the ware advertised as "90 per cent. acid proof." I also would like to state that in these series of tests all the dishes in each series were put on the hot plate at the same time and that this plate was of the type given an even temperature to all parts of the plate (see E. H. Sargent's catalog for cut of plate No. 2406). While, as stated, the

solutions were not allowed to boil vigorously, they were allowed to boil down as rapidly as possible without spattering. From eighteen to twenty minutes were required to boil to dryness.

I certainly do not advocate this as a method for testing the acid-resistance of enameled wares and agree with Mr. Staley that for a research as that seeminly indicated by my title, a constant-temperature bath and a reflux condenser should be used. However, for purposes of duplicating the treatment received by an enameled dish in actual use this method of showing the action of various acetic acid solutions might have some points in its favor over the more accurate one suggested.

A COMPARISON OF TEN WHITE ENAMELS FOR SHEET STEEL*

This paper is the record of the manufacturing and description of the physical properties of ten white enamels. It is given not with the idea of presenting to ceramic literature a set of commercial formulas, but to illustrate a method for testing, arranging the data, and arriving at the comparative values of any enamels upon which it might be desirable to experiment.

The ten enamels are those given in the "Taschenbuch für Keramiker, 1911,"[1] pages eighteen and nineteen. It should be stated, however, that some changes have been made in the milling where it was deemed necessary, and also that a feldspar high in silica has been used where the formula calls for pure feldspar.

All the materials, except the borax and the saltpeter, were finely ground. Crystals of these were used. The enamel batches were weighed, a kilogram at a time, on a balance sensitive to one hundredth of a gram. They were then very thoroughly mixed and were smelted, 200 grams at a time, in a gas-fired crucible furnace,[2] at temperatures varying from 1050° to 1200° C. This smelting required from twelve to twenty-five minutes and, as is the custom in practice, the molten enamel was poured into cold water to facilitate subsequent grinding.

The resulting frits were milled—after drying—with the required amount of tin oxide, clay, magnesia and

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* Reprinted from the Transactions of the American Ceramic Society. Vol. XIV. (Paper read at Chicago, Ill., Meeting, March, 1912.)

[1] Published by the Keramische Rundschau, Berlin, N. W., 21, Germany.

[2] See E. H. Sargent's Catalogue No. 2098 for illustration and description of this furnace.

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water, about four hundred grams at a time, in a small porcelain ball mill. (This mill is manufactured by the Abbé Engineering Co., N. Y., and is illustrated on page eleven of their catalogue.) The time required for milling varied from $3\frac{1}{2}$ to $6\frac{3}{4}$ hours.

The wet enamel from the mill was slushed upon miniature wash basins which had been previously coated with a good cobalt groundcoat. After drying and burning, a second coating of the same white enamel was applied. Both white cover-coats were applied as thin as possible and were burned in the regular muffle furnaces.

These dishes were then tested as to their resistance against corrosion by acetic acid; their behavior during rapid expansion and contraction; and their brittleness, elasticity and adhesiveness under punishment by impact; and were examined as to their opacity, gloss, etc., as a finished ware.

METHODS FOR TESTING THE WARES
Test as to Corrosion by Acetic Acid

Each dish was carefully dried and weighed correctly to 0.0001 gram; and 15 cc. of 20 per cent. acetic acid[3] (20 per cent. by volume of 99.5 per cent. acid) were measured into it. It was then placed on a gas-fired hot plate and boiled to dryness, the plate being so regulated that about thirty minutes were required to bring the vessel to dryness. The enameled dish was then washed out thoroughly with distilled water, rinsed, dried on the hot plate, cooled in a desiccator and again weighed. The difference in weight is the amount of enamel dissolved by the acid, and is recorded as "Acid Loss." The ten enamels were then arranged in a list according to their relative resistance to corrosion, the dish losing the least being first, and so on. The position of each enamel in this list is also given under "Acid Loss."

[3] This has been shown to be about the strongest mixture of acetic acid and water, as measured by its action on an enamel. See page —.

Tests of Adhesion Under Rapid Expansion and Contraction

Test 1.—Twenty-five cubic centimeters of water were heated to boiling in the dish, on a wire gauze over a Bunsen flame, and the dish was then plunged into cold water. The effect of this treatment on the enamel was recorded.

Test 2.—The dish from Test 1 was dried, heated on the wire gauze over the Bunsen flame for one minute, and then plunged into cold water and any results noted.

Test 2½.—In the dish from Test 2 a few cubic centimeters of water were boiled away—over the Bunsen flame as in the other two tests—and then the dish was allowed to remain, dry, over the flame for one minute and was again plunged into cold water. (This test may seem a duplication of the one above. It is not; many commercial wares fail with this test as it is especially severe.)

Test 3.—The dried dish from Test 2½ was very gradually heated in the blast flame until the bottom became red-hot. The results of this rapid expansion were noted.

Test 4.—While the dish was still red-hot from Test 3 it was plunged into cold water and the effect of this rapid contraction upon the enamel coating was recorded.

A description of the behavior of each enamel under these tests is given under "Expansion and Contraction," and it is to be noted that when a test is not mentioned the ware was unaffected by it. Again the enamels have been listed, this time according to their adhesiveness under rapid changes of temperature, and their position in this list is also given under "Expansion and Contraction."

Test as to Adhesion Under Punishment by Impact

A testing machine, by means of which a five-pound hammer with a three-quarter inch rounded head can be dropped twenty and one-quarter inches onto the middle of the bottom of the inverted basin, was used. The sample dishes were weighed correctly to 0.01 gram before and after the hammer was dropped upon them, and the
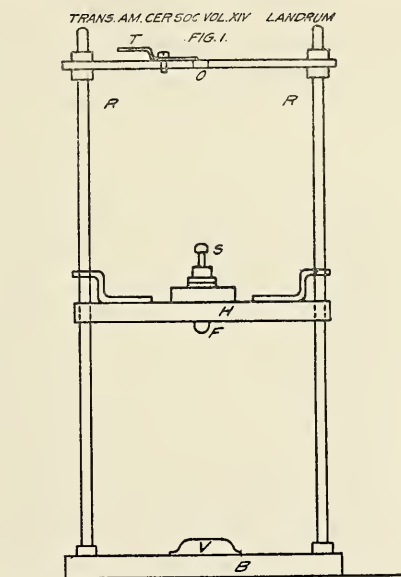
Impact Testing Machine.

grams loss and a brief description of the effect upon the enamel coating is recorded under "Loss under Hammer." As before, the enamels have been arranged in a list which shows their relative adhesion under punishment by impact.

Examination as to Opacity

The finished dishes were arranged in a series according to their opacity, and their position in this series as well as other details as to their appearance are given under "Appearance of the Ware."

Arrangement of the Data

It is the custom of the Lisk Manufacturing Company's laboratory to make a complete record of each enamel on a single sheet of special form, and although this cannot be followed exactly in publishing this article, the general arrangement and form of report will be retained.

Immediately under the heading of the enamel the batch mix in percentages and the calculated graphic formula is given, and under the latter the oxygen ratio and the ratio of the silica to the boric anhydride

Material	Formula	Equivalent weight	Loss on ignition	Cost per pound
Feldspar[4] ......0.45 Na₂O, 0.39 K₂O, 0.06 CaO, Al₂O₃, 7.11 SiO₂..		.602	1.43%	$0.0035
Borax ....Na₂O, 2B₂O₃, 10H₂O		382	47.0	0.0375
Quartz ....SiO₂		60	.....	0.0025
Cryolite 2Na₃AlF₆		420	20.0	0.0600
Soda ....Na₂O, CO₂		106	41.5	0.0085
Fluorspar ......CaF₂		78	28.2	0.0045
Calcite ....CaO, CO₂		100	43.9	0.0060
Saltpeter ......K₂O, N₂O₅		202	53.4	0.0525
Carb. magnesia..MgO, CO₂		84	52.1	0.0800
Magnesia ......MgO		40	.....	0.1000
Clay ....Al₂O₃, 2.8 SiO₂, 1.6 H₂O		300	10.0	0.0100
Tin oxide .....SnO₂		151	.....	0.4600

[4] Chemical analysis of feldspar:

	Per cent.
Silica	70.66
Alumina	16.85
Potash (K₂O)	5.93
Soda (Na₂O, by diff.)	4.61
Lime (CaO)	0.52
Carbon dioxide	0.41
Water	1.02
	100.00

(SiO_2/B_2O_3). The oxygen ratio is given considering Al_2O_3 both as a base (ORb) and as an acid (ORa). Following these ratios is the calculated loss on smelting.

BOTTOMS

INSIDES
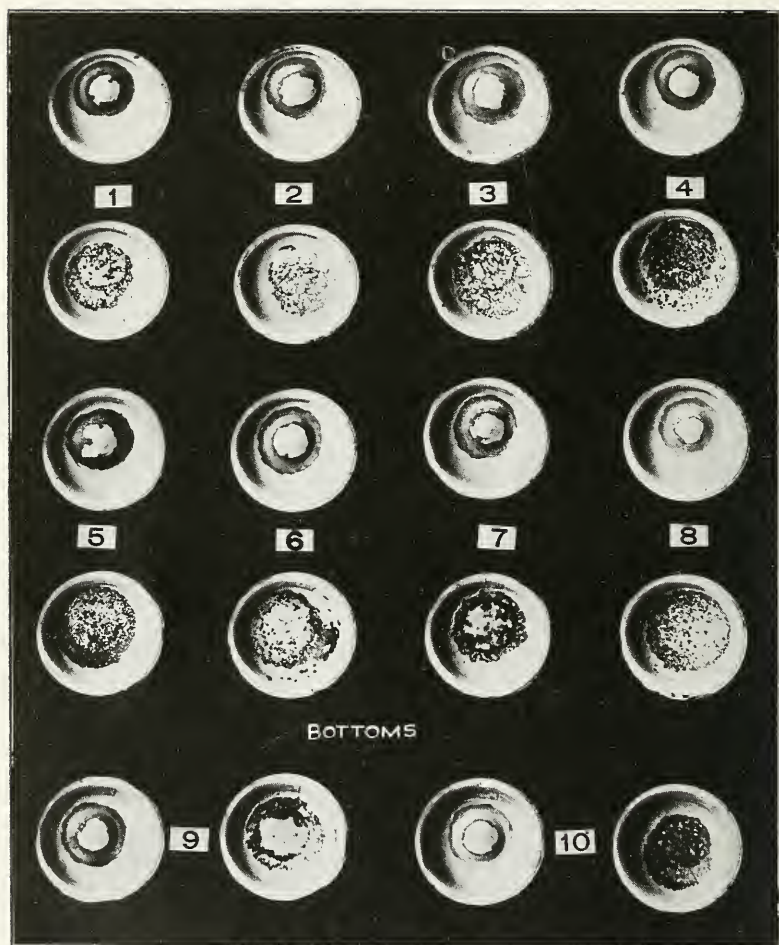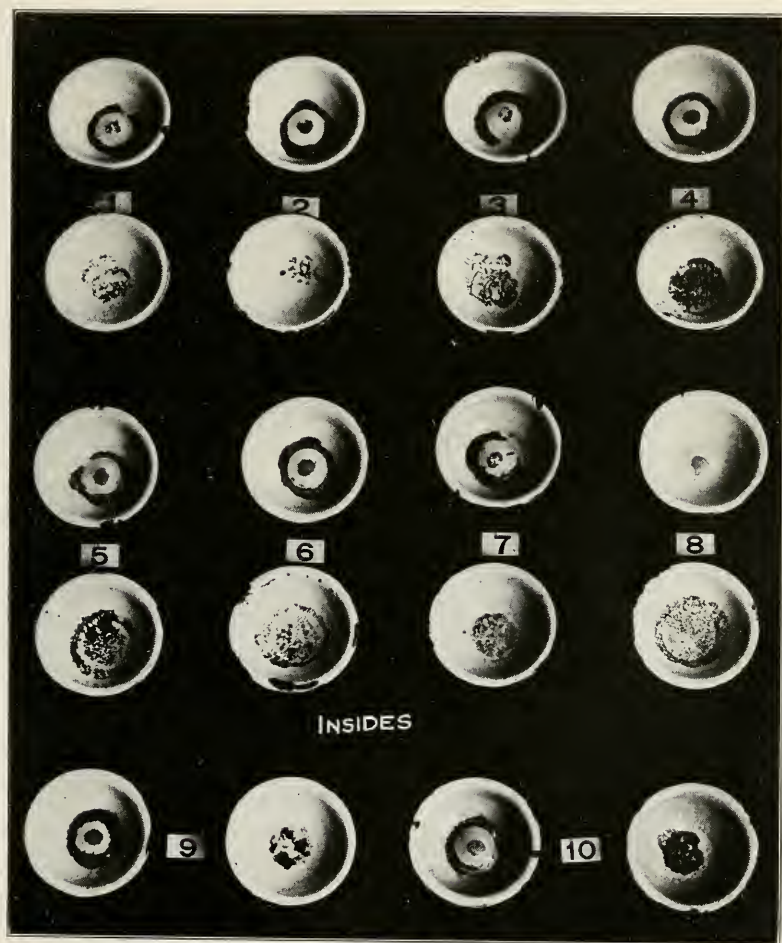
A chemical analysis of each of the materials used was made, and from them the following formulas were derived. These and the other constants given in the table above were used in making the calculations.

A brief description of the action of each enamel during smelting and of the resulting frit is given. The milling follows in percentages **of the weight of frit charged.** Thus "12 per cent. tin oxide" means "12 grams of tin oxide to each hundred grams of frit." Water is added to each milling equal to 50 per cent. of the weight of the frit.

The latter part of the record of each enamel needs no further explanation.

The Charts.—Figs. 2 and 3 show a method of arranging all the data in regard to an enamel in such a form that it may very easily be compared with any other enamel. The data of the enamels may be separated by cutting along the horizontal lines of the chart and these slips can be arranged in any order desired for making comparisons. This is especially desirable in a series where but one factor is changed at a time .

The Photographs of the Dishes.—The two half-tones show the effect of the "Hammer Test" and the "Expansion and Contraction Tests" upon both the outside and inside enamel coatings of the ten wares.

Remarks.—The types of these enamels are so different that the writer will not try to draw any conclusions. In figuring the graphic formulas the customary method has been used. In figuring the oxygen ratio, the tin oxide and the fluorine have been ignored. This is incorrect in almost every case, for it has been proved by experiment that only about 20 per cent. of the fluorine is driven off, and it is also a fact that some of the tin oxide combines to form stannous silicate. This is especially shown in Enamel X, for although this melted enamel contains 11.7

per cent. of tin oxide, it is a transparent glaze. Enamel II also illustrates this, for although its oxygen ration is 4.5 when figured in the ordinary way, it is one of the most easily smelted of the enamels under discussion.

Enamel I

Feldspar 38.6%	0.497 Na$_2$O		
Quartz 19.0	0.186 K$_2$O		2.513 SiO$_2$
Borax 15.4	0.278 CaO	0.299 Al$_2$O$_3$	0.262 B$_2$O$_3$
Cryolite 11.7	0.039 MgO		0.599 F$_2$
Saltpeter 6.5			
Calcite 6.5	ORb = 3.1 ORa = 6.7 SiO$_2$/B$_2$O$_3$ = 9.6		
Fluorspar 1.3			
Mg carbonate 1.0			

Loss on Smelting.—17.34 per cent.

Milling.—Four hours with 12 per cent. tin oxide, 7 per cent. Vallendar clay and ¼ per cent. magnesia.

Smelting.—Smelted at about 1200° C., hundred gram batches required about 15 minutes. The melted enamel is quite viscous and is inclined to be lumpy.

The Frit.—The frit is fairly opaque but is translucent in spots.

Acid Loss.—0.0101 gram (fifth in list).

Expansion and Contraction.—This ware was unaffected by heating to redness in blast flame (Test 3) and came off only over a medium sized surface on the outside and a comparatively small surface on the inside when plunged, red-hot, into cold water. This enamel is very adhesive, according to this test, and is second only to Enamel II.

Loss Under Hammer.—This was 1.07 grams, and the manner in which the enamel comes off shows it to be of average brittleness and elasticity. It is placed fifth in the list according to this test, but it is to be noticed that

FIG. 2

LANDRUM

ENAMEL	GRAPHIC FORMULA	ORb	ORa	SiO_2/B_2O_3	MILLING	LOSS IN SMELTING	COST PER HUNDRED POUNDS	OPACITY	ACID LOSS	ADHESION UNDER RAPID EXP.+CONT.	IMPACT	AVERAGE	FINAL RATING
I	.497Na₂O, .186H₂O, .278CaO, .039MgO {.251SiO₂, .299Al₂O₃, .262B₂O₃, .539F₂}	3.1	6.7	9.6	12%SnO₂ 7%Clay	17.34%	$6.70	4ᵀᴴ	5ᵀᴴ 1.01mg	2	5ᵀᴴ 1.07 gram	3ᴿᴰ	2ᴺᴰ
	38.6%	15.4%	19.0%	11.7%		1.3%	6.5%	6.5%	1.0%				
II	.563Na₂O, .131H₂O, .306MgO {.163SiO₂, .009Al₂O₃, .396B₂O₃, .525nₐ}	4.5	—	4.1	2.1%SnO₂ 4.3%SiO₂ 8%Clay	19.89%	$15.07	2ᴺᴰ	1ˢᵀ 0.0mg	1ˢᵀ	3ᴿᴰ 1.02 gram	1ˢᵀ	1ˢᵀ
	22.9%	29.7%	11.7%		1.7%	8.0%	37% 24.0%						
III	.894Na₂O, .097H₂O, .474Al₂O₃, .009CaO {.217SiO₂, .632B₂O₃, .309nₐ}	4.4	6.8	3.5	10%Clay	21.08%	$9.81	7ᵀᴴ	2ᴺᴰ 0.16mg	3ᴿᴰ	9ᵀᴴ 1.31 gram	4ᵀᴴ	4ᵀᴴ
	22.0% 30.0%	17.5%	13.5%		2.0%	1.50%							
IV	.834Na₂O, .089H₂O, .007CaO, .061MgO {.257SiO₂, .040Al₂O₃, .772B₂O₃, .721F₂}	3.4	6.8	9.5	6.67%SnO₂ 4.44%Clay	16.61%	$5.03	5ᵀᴴ	3ᴿᴰ 3.3mg	10ᵀᴴ	6ᵀᴴ 1.07 gram	9ᵀᴴ	5ᵀᴴ
	23.5% 16.2%	31.4%	15.7%	9.3%		2.0%	7.0%	3.1%	0.8%				
V	.504Na₂O, .176H₂O, .320CaO {.244SiO₂, .281Al₂O₃, .284B₂O₃, .636F₂}	3.1	6.6	8.6	11.76%SnO₂ 5.88%Clay	17.86%	$6.67	3ᴿᴰ	4ᵀᴴ 8.4mg	6ᵀᴴ	2ᴺᴰ 1.08gram	5ᵀᴴ	3ᴿᴰ
	35.3% 16.8%	20.5%	12.0%		2.0%	6.4%							

Column ingredients (bottom labels): TIN OXIDE, MAGNESIA, MgCO₃, SALTPETER, CALCITE, FLUOR.SPAR, SODA, CRYOLITE, QUARTZ, BORAX, FELDSPAR

All enamels smelted at 1050° to 1200° centigrade for from 12 to 25 minutes. All millings include 2% MgO

FIG. 3

ENAMEL	GRAPHIC FORMULA	ORb	ORa	SiO₂/B₂O₃	MILLING	LOSS IN SMELTING	COST PER HUNDRED POUNDS	OPACITY	ACID LOSS	ADHESION RAPID CONT.EXP	ADHESION IMPACT	AVERAGE	FINAL RATING
VI	.648 Na₂O / .109 K₂O } .198 Al₂O₃ { .558 SiO₂ / .452 F₂ / .225 B₂O₃ ; .243 CaO	2.7 (32.0%)	5.0 (26.0%)	3.8 (8.0%)	93% SnO₂, 7% Clay (5.0%)	20.11% (9.0%)	$11.10 (6.0%)	1ST	8TH, 19.0mg (3.0%)	7TH (10%)	8TH, 1.13gram (1.10%)	7TH	6TH
VII	.500 Na₂O / .179 K₂O } .304 Al₂O₃ { .525 SiO₂ / .598 F₂ / .258 B₂O₃ ; .282 CaO / .039 MgO	3.0 (38.0%)	6.7 (15.0%)	9.9 (19.0% / 12.0%)	11.1% Clay	17.09% (1.0%)	$2.17 (7.0%)	9TH	9TH, 20.4mg (6.0%)	9TH (10%)	4TH, 1.06gram	8TH	9TH
VIII	.661 Na₂O / .111 K₂O } .204 Al₂O₃ { .508 SiO₂ / .293 F₂ / .463 B₂O₃ / .215 F₂ ; .228 CaO	2.7 (38.4% / 27.8%)	5.0	3.3 (13%)	7.87% SnO₂, 4.5% Clay	20.87% (1.13%)	$12.08 (5.3%)	6TH	10TH, 353mg (2.0%)	4TH	1ST, 0.56gram (13.9%)	2ND	8TH
IX	.670 Na₂O / .082 K₂O } .284 Al₂O₃ { .240 SiO₂ / .834 F₂ / .323 B₂O₃ ; .005 CaO / .263 MgO	3.4 (17.7%)	6.5 (20.5%)	7.4 (36.3%)	10% Clay (19.4%)	15.48% (1.8%)	$2.87 (6.3%)	8TH	7TH, 15.9mg (.9%)	8TH	10TH, 1.42gram (3.5%)	10TH	10TH
X	.841 Na₂O / .142 K₂O } .284 Al₂O₃ { .203 SiO₂ / .279 F₂ / .625 B₂O₃ ; .005 CaO / .017 CaO / .263 MgO	3.2 (45.7% / 32.0%)	6.8	3.2	6.4% Clay	21.33% (1.4%)	$7.01 (14%)	10TH	6TH, 11.9mg (1.7%)	5TH	7TH, 1.09gram (9.2%)	6TH	7TH

Batch ingredient columns (right axis): TIN OXIDE, MAGNESIA, MgCO₃, SALTPETER, CALCITE, FLUOR SPAR, SODA, CRYOLITE, QUARTZ, BORAX, FELDSPAR

Hammer weighing 5 lbs. and falling 20¼ inches used in Impact Test. 20% Acetic acid used in Acid Test.

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all the enamels, excepting VIII, which is much the best, and IX and III, which are much the worst, stand very close together.

Appearance of the Ware.—This ware sets a very high standard in its appearance and is much more opaque than many with higher tin oxide content. In fact, it would be marketable with a much smaller proportion of this oxide added at the mill, and with this change would be a good commercial enamel. As it stands, it is fourth in the list, according to opacity.

Cost.—The cost of the materials for the finished enamel is $6.70 per hundred pounds; and this could be reduced by using less potassium nitrate, and, as said before, by using less tin at the mill.

Remarks.—If the cost is not considered, but considering everything else, this is the second best enamel of the ten. If cost is considered, it is the **very best.**

<div align="center">Enamel II</div>

Quartz 29.7%	$0.563 \, Na_2O$		$1.636 \, SiO_2$
Tin oxide 24.0	$0.131 \, K_2O$		$0.396 \, B_2O_3$
Borax 22.9	$0.306 \, MgO$		$0.525 \, SnO_2$
Sodium carbonate 11.7			
Saltpeter 8.0	$OR = 4.5 \; SiO_2/B_2O_3 = 4.1$		
Magnesia 3.7			

Loss on Smelting.—19.89 per cent.

Milling.—Six and three-fourths hours with 4.3 per cent. quartz, 2.1 per cent. tin oxide and 8 per cent. Vallendar clay.[5]

Smelting.—Smelted at about 1200° C., hundred gram batches required about 15 minutes. To get the maximum opacity it was necessary to mechanically stir just before pouring. The viscosity was medium and melt was free from lumps.

The Frit.—The frit was extremely opaque and quite hard and tough.

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[5] Necessary for correct slushing but not given in original directions.

Acid Test.—The acid test showed this enamel to be absolutely unaffected by 20 per cent. acetic acid solutions, and thus it is first in the list as to resistance to corrosion by acid.

Expansion and Contraction.—When plunged, red-hot, into cold water (Test 4) this enamel came off over very small surfaces, both inside and outside, and in such a manner that it is easily singled out as the most adherent enamel of the ten. Few enamels have ever been tested by the writer that have withstood sudden changes of temperature as well as this one.

Loss Under Hammer.—This was 1.02 grams. This enamel is of average brittleness and elasticity and is placed third in the list as to adhesion under punishment by impact, but an examination of the sample used for this test shows that it is not as well suited to the ground coat as is Enamel I.

Appearance of Ware.—This ware is very opaque, and it certainly should be, as the finished enamel contains something like 32 per cent. of tin oxide. It is second in opacity only to Enamel VI, which contains a little over 23 per cent. of tin oxide when on the ware. This enamel is so opaque that it may be put on in very thin coatings. This is an advantage, as the thinner the enamel is applied the more durable the product.

Cost.—The cost of this enamel is $15.07 per hundred pounds, and this would make it entirely impractical to use on a commercial ware. It is a freak enamel in every sense, and is of interest on this account.

Enamel III

Borax 30.0%	0.894 Na_2O		2.217 SiO_2
Feldspar 22.0	0.097 K_2O	0.147 Al_2O_3	0.632 B_2O_3
Quartz 17.5	0.009 CaO		0.399 SnO_2
Tin oxide 15.0			
Sodium carbonate .13.5	ORb = 4.4 ORa = 6.8 SiO_2/B_2O_3 = 3.5		
Saltpeter 2.0			

Loss on Smelting.—21.08 per cent.

Smelting.—Smelted at about 1200° C. for 15 minutes or less; the melt pours with medium viscosity.

The Frit.—The frit was creamy-white and very opaque. Some of the tin oxide remained in suspension, but, except for this, the frit was homogeneous.

Milling.[6]—Five hours with 10 per cent. Vallendar clay, and ¼ per cent. magnesium oxide.

Acid Loss.—The acid loss was but 0.0016 gram. This is remarkably low and places this enamel second in the list as to acid resistance.

Expansion and Contraction.—This too is an excellent enamel, according to the manner in which it withstands punishment by rapid changes of temperature. It was unaffected by any of the tests up to Test 4 and when plunged, red-hot, into water during this test came off in flakes, both from the inside and outside of the dish. Very little steel was laid bare, but the surface of the ground coat enamel which was exposed is larger than on either Enamel I or Enamel II. This enamel is placed third on the list.

Loss Under Hammer.—This was 1.31 grams. This shows up the chief fault in this enamel—brittleness and lack of elasticity—and places it next to last in the list, arranged in accordance with their relative ability to withstand punishment by impact.

Appearance of Ware.—Considering the fact that this enamel contains about 19 per cent. of tin oxide when on the ware, it is very poor in opacity indeed. The writer has made many white enamels with no other opacifier than cryolite that were more opaque than this one. It is fourth from the poorest among these ten.

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[6] Original directions gave no milling.

Cost.—The cost of this enamel is $9.81 per hundred pounds. If the cost is not considered, this enamel stands fourth, considering all its properties.

<div align="center">

Enamel IV

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Quartz ....31.40% 0.834 Na_2O ⎫ ⎧ 2.571 SiO_2
Feldspar ....23.50   0.098 K_2O ⎪ 0.249 Al_2O_3 ⎨ 0.272 B_2O_3
Cryolite ......15.70   0.007 CaO   ⎬   ⎩ 0.721 F_2
Borax ....16.20   0.061 MgO   ⎭
Sodium carbonate. 9.30
Saltpeter ...... 3.10   ORb = 3.4 ORa = 6.8 SiO_2/B_2O_3 = 9.5
Magnesia 0.80

Loss on Smelting.—16.61 per cent.

Smelting.—Smelted at about 1100° C., four hundred

gram batches required 15 minutes. The viscosity of the melt was medium.

The Frit.—The frit had little, if any, opacity and with a smelting of 18 minutes became a clear glass.

Milling.—Four hours with 6.67 per cent. tin oxide, 4.44 per cent. Vallendar clay, and ¼ per cent. magnesia.

Acid Loss.—0.0033 gram, placing this enamel third on the list.

Expansion and Contraction.—While being heated to dryness (Test 2½) innumerable "nail chips" flew off, both from the inside and outside surface, and when heated to redness in the blast flame (Test 3) a few more came off. When plunged red hot into cold water (Test 4) the coatings peeled off over medium sized surfaces, leaving the ground coat almost bare. Notwithstanding the apparent adhesiveness under Tests 3 and 4, the utter failure of this enamel under Test 2½ causes it to be deemed the poorest of the ten, according to its resistance to punishment by rapid changes of temperature.

Loss Under Hammer.—This was 1.07 grams; and although this is not far different from several others, the

manner in which the remaining enamel adhered places this ware sixth in the list.

Appearance of the Ware.—Although this enamel contains but eight per cent. of tin oxide in its finished coating, it is opaque enough to be placed fifth in the list. The gloss is quite poor.

Cost.—The cost of this enamel is $5.03 per hundred pounds. Its final rating places it fifth in the list.

Enamel V

Feldspar 35.30%	0.504 Na_2O			⌈ 2.447 SiO_2
Quartz 20.50	0.176 K_2O	⎫ 0.281 Al_2O_3	⎨ 0.284 B_2O_3
Borax 16.80	0.320 CaO	⎬	⎩ 0.636 F_2
Cryolite 12.00	⎭		
Calcite 7.00	ORb = 3.1 ORa = 6.6 SiO_2/B_2O_3 = 8.6		
Saltpeter 6.40			
Fluorspar 2.00			

Loss on Smelting.—17.86 per cent.

Smelting.—Smelted at about 1100° C., in from 18 to 20 minutes. The melt, when poured, was very thick and sticky. This mixture is inclined to melt unevenly and should be mechanically stirred for best results.

The Frit.—The frit has a translucent white color, fairly good for the amount of cryolite it contains. It is not noticeably hard and tough.

Milling.—Five hours with 11.76 per cent. of tin oxide, 5.88 per cent. of Vallendar clay, and ¼ per cent. magnesia.

Acid Loss.—0.0084 gram. This is of about the same acid resistance as the best wares on the market and is excelled only by Enamels I, II and IV in this list.

Expansion and Contraction.—When boiled to dryness on asbestos gauze, this enamel chipped slightly (Test 2½) but was not further affected when plunged

into cold water. When heated to redness (Test 3) more chips flew off the outside and the inside enamel blistered somewhat. When plunged, red hot, into cold water according to Test 6, the enamel came off very badly from both surfaces of the dish, and much steel was laid bare. This enamel stands sixth according to this test, and is typical of the action of many of the wares on the market.

Loss Under Hammer.—This was 1.00 gram, showing this enamel to be quite elastic. It stands next to the best, according to this test.

Appearance of the Ware.—This ware is quite opaque, standing third among the ten, but when one considers that 12 per cent. of cryolite was used in the smelt and that the finished enamel contains 12 per cent. of tin oxide, he comes to the conclusion that much of the color must have been lost.

Cost.—The cost of this enamel is $6.67 per hundred pounds and its final rating places it third best, when all its physical properties are considered.

Enamel VI

Feldspar 32.00%	0.648 Na₂O		⌈1.558 SiO₂
Borax 26.00	0.109 K₂O	0.198 Al₂O₂	0.415 B₂O₃
Tin oxide 11.00	0.243 CaO		0.452F₂
Sodium carbonate. 9.00			⌊0.222 SnO₂
Quartz 8.00			
Fluorspar 6.00	ORb = 2.7 ORa = 5.0 SiO₂/B₂O₃ = 3.8		
Cryolite 5.00			
Saltpeter 3.00			

Feldspar 32.00%
Borax 26.00
Tin oxide 11.00
Sodium carbonate. 9.00
Quartz 8.00
Fluorspar 6.00
Cryolite 5.00
Saltpeter 3.00

$0.648\ Na_2O$
$0.109\ K_2O$
$0.243\ CaO$

$0.198\ Al_2O_2$

$1.558\ SiO_2$
$0.415\ B_2O_3$
$0.452F_2$
$0.222\ SnO_2$

$ORb = 2.7 \quad ORa = 5.0 \quad SiO_2/B_2O_3 = 3.8$

Loss on Smelting.—20.71 per cent.

Smelting.—Smelted at about 1150° C. in from 20 to 22 minutes. The viscosity of this enamel was rather low.

The Frit.—The frit was creamy-white and quite opaque but inclined to be non-homogeneous. Threads of this enamel were brittle.

Milling.—Five hours with 9.3 per cent. tin oxide, 7 per cent. Vallendar clay, and ¼ per cent. magnesia.

Acid Loss.—0.0190 gram, placing this enamel eighth on that list.

Expansion and Contraction.—During Test 3 a few large chips came off while the dish was being heated to redness in the blast flame. When plunged red-hot into cold water, a large surface of the ground coat was laid bare on the outside, but the inside was affected very much less. This enamel is seventh best, according to this test.

Loss Under Hammer.—This is 1.13 grams, which is the average, but places this enamel third from the last when listed according to its relative resistance to punishment by impact.

Appearance of the Ware.—This is the best appearing enamel of the ten, and its great opacity is not to be wondered at when we consider that as a finished enamel it contains about 23 per cent. of tin oxide. The gloss is splendid.

Cost.—The cost of this enamel is $11.10 per hundred pounds; but as much more oxide of tin has been used than is necessary for even a very high grade ware, this could be greatly reduced. Considering everything, this is the sixth best enamel of the ten.

Enamel VII

Feldspar	39.00%	0.500 Na_2O			2.525 SiO_2
Quartz	19.00	0.179 K_2O			0.255 B_2O_3
Borax	15.00	0.282 CaO	0.303 Al_2O_3		0.598 F_2
Cryolite	12.00	0.039 MgO			
Calcite	7.00				
Saltpeter	6.00	ORb = 3.0 ORa = 6.7 SiO_2/B_2O_3 = 9.9			
Fluorspar	1.00				
Mg carbonate	1.00				

Loss on Smelting.—17.09 per cent.

Smelting.—Smelted at about 1200° C. The melt poured thin and somewhat lumpy.

The Frit.—The frit was quite translucent and non-homogeneous, a hard glassy frit.

Milling.—Three and one-half hours with 11.1 per cent. Vallendar clay and ¼ per cent. magnesia.

Acid Loss.—0.0204 gram, or next to the worst in the ten.

Expansion and Contraction.—This enamel chipped somewhat when boiled to dryness in Test 2½, but no more chipping was observed while heating to redness in blast flame (Test 3). When plunged, red-hot, into cold water (Test 4) the enamel adhered fairly well, especially on the inside, but the failure in Test 2½ places this enamel next to the poorest, according to this test.

Loss Under Hammer.—This was 1.06 grams and this ware comes fourth as to its adhesiveness under punishment by impact.

Appearance of Ware.—Considering the fact that there is no oxide of tin in this enamel, it is quite opaque indeed and deserves further trial with tin oxide added at the mill. Even as it stands, it is more opaque than Enamel X, which contains almost 12 per cent. of tin oxide. It stands next to the last in the list, arranged according to the relative opacity of the ware.

Cost.—On account of the absence of tin oxide in the make-up of this enamel, its cost is but $2.17 per hundred pounds. With the proper addition of this oxide at the mill, this enamel would cost about $5.00 per hundred pounds. Everything except the cost considered, this enamel is rated as ninth best.

Enamel VIII

Feldspar 38.40%	0.661 Na$_2$O		1.509 SiO$_2$
Borax 27.80	0.111 K$_2$O	0.203 Al$_2$O$_3$	0.463 B$_2$O$_3$
Tin oxide 13.90	0.228 CaO		0.215 F$_2$
Sodium carbonate 11.30			0.293 SnO$_2$
Fluorspar 5.30			
Saltpeter 2.00	ORb = 2.7 ORa = 5.0 SiO$_2$/B$_2$O$_3$ = 3.3		
Quartz 1.30			

Loss on Smelting.—20.87 per cent.

Smelting.—Smelted at about 1200° C. for from 15 to 18 minutes. The viscosity was rather low. Although the melting point of this enamel is low, it was difficult to drive off all the CO_2.

The Frit.—The frit was creamy and very opaque, but rather brittle.

Milling.—Four hours with 7.87 per cent. tin oxide, 4.5 per cen. Vallendar clay, and ¼ per cent. magnesia.

Acid Loss.—0.0353 gram. This is entirely too high for a cooking utensil and places this ware last in the list as to its resistance to corrosion by acetic acid.

Expansion and Contraction.—While heating this dish to redness, a few chips flew off and when plunged, red-hot, into cold water (Test 4) the enamel flaked off over quite a large surface, but only to the ground coat and even this was fairly well covered by the adhering cover coat. This ware stands fourth according to this test.

Loss Under Hammer.—This was 0.56 gram, so that according to this test the enamel is very excellent indeed. It stands punishment by impact better than any of the rest.

Appearance of Ware.—The opacity of this ware is very low, considering the fact that it contains 25½ per cent. of tin oxide. It stands sixth when listed according to opacity.

Cost.—The cost of this ware is $21.08 per hundred pounds. This is the most expensive of the wares, except one, and yet it stands sixth according to opacity and eighth when everything is considered.

Quartz ....35.30%   0.670 Na$_2$O
Borax ....20.50   0.062 K$_2$O
Cryolite ......19.40   0.005 CaO   } 0.228 Al$_2$O$_3$ { 2.406 SiO$_2$
Feldspar ......17.70   0.263 MgO   0.323 B$_2$O$_3$
Magnesia ...... 3.50   0.834 F$_2$
Sodium carbonate 1.80   ORb = 3.4 ORa = 6.5 SiO$_2$/B$_2$O$_3$ = 7.4
Saltpeter 1.80

Loss on Smelting.—15.48 per cent.

Smelting.—Smelted at about 1200° C. for from 15 to 18 minutes. This enamel was difficult to pour from the crucible. The enamel was quite viscous and lumpy.

The Frit.—The frit was very hard and, although quite opaque, was translucent in spots.

Milling.[7]—Three and a half hours with 10 per cent. Vallendar clay and ¼ per cent. magnesia.

Acid Loss.—0.0159 gram, or seventh in the list of ten enamels.

Expansion and Contraction.—When plunged, red-hot, into cold water (Test 4) this enamel came off over a large surface on the outside and a small surface on the inside of the dish. The steel was laid bare in many places. In the list of wares, arranged according to their resistance to punishment by change of temperature, this enamel stands eighth, as it scaled slightly during Test 2½ when water was boiled to dryness in it.

Loss Under Hammer.—This was 1.42 grams, which is more than any of the other dishes lost, and places this enamel last in the list.

Appearance of Ware.—This enamel is remarkable in its opacity, all of which comes from the cryolite and clay. It contains no tin oxide and stands eighth in the list according to opacity.

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[7] Milling not given in original directions.

Cost.—The cost is but $2.87 per hundred pounds. With sufficient oxide added at the mill to bring this up to a remarkable standard, this enamel would cost about $5.50 per hundred pounds. Considering everything, this is the poorest enamel of the ten.

Enamel X

Feldspar 45.70%	0.841 Na_2O			2.013 SiO_2
Borax 32.00	0.142 K_2O	}	0.283 Al_2O_3 {	0.625 B_2O_3
Sodium carbonate 11.40	0.017 CaO			0.227 SnO_2
Tin oxide 9.20				
Saltpeter 1.70	ORb = 3.2 ORa = 6.8 SiO_2/B_2O_3 = 3.2			

Loss on Smelting.—21.33 per cent.

Smelting.—Smelted at about 1050° C. for 20 minutes; this enamel became transparent, although it contains 9.2 per cent. tin oxide. Its viscosity was medium.

The Frit.—The frit was a colorless glass, comparatively hard and quite tough.

Milling.—Four and one-fourth hours with 6.4 per cent. Vallendar clay and ¼ per cent. magnesia.

Acid Loss.—0.0119 gram, placing this enamel sixth in the list.

Expansion and Contraction.—While heating to redness in the blast flame, the enamel bubbled slightly, and when plunged, red-hot, into cold water, came off to the steel over a small surface on the inside and a larger surface on the outside. This enamel stands fifth, according to this test.

Loss Under Hammer.—This was 1.09 grams, which places this cover coat seventh in the list.

Appearance of Ware.—Although this enamel contains 11.7 per cent. tin oxide, it stands last in opacity, being nothing more nor less than a clear glass.

Cost.—The cost of this enamel is $7.01 per hundred pounds.

Discussion

MR. RANKIN: Mr. Landrum, I would like to ask if you have ever made any experiments in the line of substituting sodium nitrate for potassium nitrate?

MR. LANDRUM: I have made experiments on a small scale and a large scale. The substitution of sodium nitrate for potassium nitrate is successful only where you can make routine analyses of the sodium nitrate. Sodium nitrate takes up water from the air, and thus varies in strength. In the sheet steel enameling industry, the variation of water content will spoil the enamel unless this is taken into account.

I worked in one place where they determine this very nicely by weighing about ten or fifteen pounds and then drying and reweighing it, thus getting results which were as accurate as taking a smaller sample and testing it in the laboratory.

MR. STALEY: I wish to say that I consider this a very able paper.

The Germans do not use the empirical formula in their enamel industries to any large extent. They publish their results in percentage of the various oxides. When it comes to fluorides, they publish their results in percentage of the various fluorides. I think that is a fairly good way. In my own papers, I prefer to consider the melted weights of the various minerals; consider the feldspar, for instance, as feldspar rather than as split up into the oxides. The method I use is very similar to that of the Germans. Mr. Landrum advocates the use of empirical formulas in connection with batch weights. This divergence in methods of calculation shows very nicely that, provided a man works in a systematic manner and has enough experience, he can get results from a variety of methods of calculation.

Enamels III and X are two cases where there are high sodium and potassium oxides and practically no

other basic oxide. I believe that early in the history of this Society Mr. Burt gave the results of some experiments in which he showed that you can melt tin oxide and sodium carbonate, or tin oxide and potassium carbonate, together and get a clear glass. It is known that there are sodium stannates and potassium stannates in existence which are translucent. I think it is more plausible to say that in a material as basic as enamel the loss in opacity is due to the fact that the potash and soda are high rather than to attribute the poor opacity to any hypothetical effect that the alkaline earths have in preventing the tin from forming stannous silicate. I have always found that, with a given amount of tin oxide, when sodium and potassium run up the opacity decreases. To verify Mr. Landrum, I find that increasing calcium or barium oxide increases the opacity. To my mind this means simply that opacity was increased by decreasing the percentage of sodium and potassium.

MR. PURDY: I would like to ask Mr. Landrum if it makes any difference in the power of tin oxide to produce opacity, whether you frit it or use it raw?

MR. LANDRUM: Yes, there is a very marked difference. This has already been brought out in the Transactions. It never pays to put tin oxide in the smelt for opacity.

I have found, however, that it is good practice to put a small amount of tin oxide in the smelt for gloss. In this case you get no opacity from the tin oxide. For maximum color, the tin oxide should be added at the mill.

THE NECESSITY OF COBALT OXIDE IN GROUND-COAT ENAMELS FOR SHEET STEEL*

There has been a great deal of discussion recently in German ceramic literature over the function of the ground coat and especially as to the necessity of cobalt being present in such an enamel. As the durability of an enameled ware is primarily dependent upon the physical properties of this fundamental coating, it might be well to review what has been said upon the subject.

In the Transactions of the American Ceramic Society, XI, p. 115, J. B. Shaw says that cobalt-containing grounds have the advantage that they change color during burning, the iron taken up from the steel destroying the blue cobalt color. "The ground coat is considered well burnt when the blue color is no longer visible. It seems to be quite generally believed that CoO has a great affinity for iron and that a good ground coat cannot be made without using CoO." Shaw goes on to say that from his experiments along this line he feels perfectly safe in stating that this belief is ungrounded.

About the only other time that this subject is mentioned in the Transactions is by J. H. Coe, Volume XIII, p. 549, and he states that the value of cobalt oxide in the ground coat for cast iron is doubtful.

Dr. Grunwald in his book "Enameling on Iron and Steel," p. 22, says: "Cobalt oxide possesses valuable physical characteristics which make it suitable for the preparation of ground (coat) enamels, for these derive the property that their coefficients of expansion are as near as possible the same as sheet iron." This is disputed by M. Mayer and B. Havas[1] who find that ground coat

[1] Chem. Ztg. Vol. XXXIII, p. 1314.

enamels have a much lower coefficient of expansion than that of sheet steel.

Dr. Vondracek, in the Sprechsaal, 1909, No. 14, seems to have first propounded the theory of the function of cobalt in a ground-coat enamel which is most popular at present. He considers that the iron, at the melting temperature of the ground coat, is oxidized at the expense of the cobalt oxide and that the latter, or rather the cobalt silicate, is changed to a compound of lower oxygen content, or is even reduced to the metal. As a result of this, the clean surface of the iron is attacked so that the enamel joins very intimately with the metal and the danger of the chipping off of the enamel coats is lessened. In another place, Dr. Vondracek, although he repeats that cobalt improves the adhesiveness of enamels, says: "I have, notwithstanding, often obtained a very adhesive ground-coat enamel without using cobalt oxide."[2]

Philip Eyer in his book "Die Eisenemailierung," pp. 10-12, says: "The idea of adding cobalt oxide to the glaze so that it will go into combination with the iron is faulty, for a good, adherent ground-glaze can be prepared without the use of that oxide. However, the application of such a ground coat is impossible in practice." Also in writing of cast-iron enamels in the "Glashutte," Vol. XLI, pp. 737-8, 764-5, he says that cobalt and nickel are necessary as they form a weak alloy with the iron.

C. Tostman, in the Keramische Rundschau, XIX, pp. 5, 65 and 107, discusses this subject and emphasizes especially, what is, in the writer's opinion, the best argument as to the necessity of cobalt in a ground coat. He agrees with Shaw that cobalt acts as an indicator for correctly burning the enamel. He says in part:

"Only in cobalt oxide grounds does a blue color appear on smelting. If one should discontinue the heating just at this point, it would not adhere firmly enough to the steel, even though it had already become molten and glass-like. One can also burn it so long

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[2] See Chem. Ztg., XXX, 575-7.

that the color becomes black. Now how is this (definite) color change, which is so markedly essential for a proper adhesion, to be explained? The only explanation I find for it is that the enamel has taken up the iron from the surface (of the black shape) in some form of oxidation."

He goes on to state that while this oxygen might come from the air in the muffle, it is more probable that it is given up by the oxide of cobalt, which is in turn reduced to metal. "These small amounts of very finely divided metallic cobalt could then perhaps form a very porous alloy with the iron on the surface of the shape. To this, the enamel would be able to adhere firmly, while the silicate flux would take the place of the cobalt which alloyed with the iron." He gives as an argument that this oxygen is furnished to the iron by the cobalt and not from any other source, the fact that in ground coats, which are not colored by cobalt, "an exceedingly smaller change of color takes place during the burning." He also mentions the fact that the addition of borax to an enamel causes it to chip and the further addition of cobalt oxide seems to correct this.

Dr. Bela Havas[3] replies to Tostman that he agrees with him that the cobalt silicate in the ground coat is reduced to a lower stage of oxidation and, as previously published by him in coöperation with M. Mayer,[4] this is indicated by the change of color of the enamel coating from blue to green. However, he states that it is improbable that the reduction of the cobalt silicate at the temperatures involved would go far enough to produce metallic cobalt.

The writer has no new theories to offer, but he is very strongly of the opinion that cobalt is a necessary ingredient in a successful ground coat for two reasons, which have been given above:

First, it is an excellent indicator which will inform the "burner" exactly the point at which his charge of ware is correctly burned.

[3] Sprechsaal XLIV 72-3.
[4] Ibid., XLIII, 727-9.
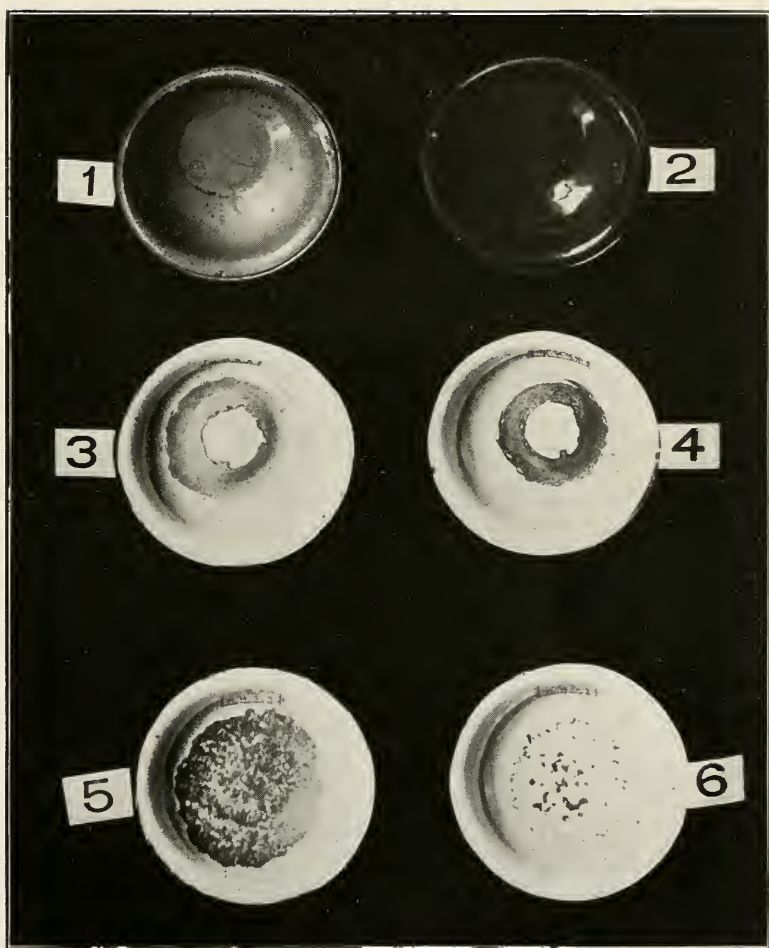
Fig. 1

Second, whatever may be the reason, the fact remains that cobalt grounds adhere more firmly to the steel than those not containing this metal, and it is the opinion of the writer that any non-cobalt ground coat can be improved in its adhesive properties by the correct addition of cobalt to its formula.

To illustrate this a ground coat was prepared which is practically a transparent glaze. When it is coated on a piece of ware the bright steel surface shows through the glaze and makes this appear a very light colored coating (see Fig. I, 1). The composition is practically the same as that of the Mayer and Havas ground No. 1 as given in the Sprechsaal, 1909, No. 34.

M-H. Ground Coat Number One[5]

Batch mix		Graphic formula		
Feldspar 36.34%	0.642 Na$_2$O			
Borax 35.64	0.0802K$_2$O			2.256 SiO$_2$
Quartz 14.38	0.243CaO	0.204 Al$_2$O$_3$		0.231 F$_2$
Soda 7.42	0.025 MnO			0.629 B$_2$O$_3$
Fluorspar 5.34	0.010 CoO			
Manganese oxide. 0.65				
Cobalt oxide 0.23	ORb 4.0, ORb 7.0, SiO$_2$/B$_2$O$_3$ 3.6			

Milled with 6 per cent. clay and 2½ per cent. dissolved borax.

A cobalt ground coat has been prepared which has the same chemical composition except that 0.03 equivalent part of CaO has been replaced by 0.03 equivalent part of CoO (see Fig. I, 2). This enamel has been made as follows:

Cobalt Ground Coat[5]

Batch mix		Graphic formula		
Feldspar 36.42%	0.642 Na$_2$O		2.260 SiO$_2$
Borax 35.54	0.080 K$_2$O		
Quartz 14.38	0.213 CaO	0.203 Al$_2$O$_3$	0.628 B$_2$O$_3$
Soda 7.42	0.040 CoO		
Fluorspar 4.64	0.025 MnO		0.201 F$_2$
Manganese oxide. 0.65			
Cobalt oxide 0.95	ORb 4.0, ORa 7.0, SiO$_2$/B$_2$O$_3$ 3.6		

[5] The same materials and method of manufacturing and a similar arrangement of data have been used as in "Comparison of Ten White Enamels for Sheet Steel," this volume.

Milled with 6 per cent. clay and 2½ per cent. dissolved borax.

Each of these enamels has been coated with two white cover coats and then tested under the hammer (see article on white enamels), and it is to be noticed that the non-cobalt ground coat leaves the steel entirely bright and bare (see Fig. I, 3), while the one containing cobalt still adheres in concentric ridges (see Fig. I, 4). It is very evident that the cobalt must cause this extra adhesiveness.

Discussion

MR. LANDRUM: As an example of the reduction of a metal oxide (or silicate) in an enamel coating by the steel of the shape it may be interesting to examine a sample dish coated with the following enamel:

0.451 Na_2O			
0.019 K_2O			0.886 SiO_2
0.123 CaO	0.111 Al_2O_3		0.282 B_2O_3
0.285 ZnO			
0.122 CuO			0.123 F_2
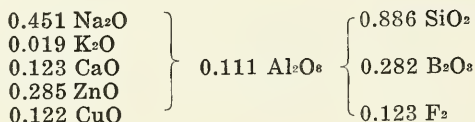
Milled with 6½ per cent. clay.

This enamel when used as a cover coat (separated from the steel by a ground-coat enamel) is **green** but when applied directly to the steel becomes **red** through the reduction of the copper compound. It may be observed on the sample which has been dented in the testing machine that some of the copper compound has been reduced to the metal and that this is plated on the steel surface.

MR. PURDY: You have tried oxides other than cobalt? Have you tried nickel, for instance?

MR. LANDRUM: I have tried oxide of nickel and it works fairly well, but does not promote adhesiveness to as great a degree as does the oxide of cobalt. It is best used in combination with that oxide.

MR. PURDY: There is no actual oxygen for it to give up.

MR. LANDRUM: We have nickelic and nickelous compounds, and the change may be from one to the other and not necessarily a change of the oxides; then, too, the conclusion might be drawn that the reduction is to metallic nickel. In the case of the enamels under discussion, it is easy to see that the one containing cobalt (see vessel 4 in illustration) **does** adhere to the steel after being dented while the one which does not contain cobalt (vessel 3) **does not** adhere but leaves the steel surface bright.

PROF. STALEY: You will have to look at it with a microscope.

MR. LANDRUM: I have examined this and other cobalt grounds under the microscope and have not been able to see any evidence of an alloy being present. The dark particles remaining after the dish is dented have a gloss that would lead one to think that they are particles of the glaze rather than of metal. Microscopic examination is difficult as it is practically impossible to get a good cross section of an enameled steel sheet.

PROF. STALEY: In other words, this alloy theory is used just because it fits in—because it is within reason?

MR. LANDRUM: Yes, and even then there is a doubt that it is within reason at enameling temperatures.

MR. PURDY: In our transactions I stated as my opinion that cobalt in the ground coat merely furnished a mechanical means of holding the enamel onto the iron. It is easy to enamel most metals directly, but very difficult to enamel iron. The cobalt is merely suspended in the ground coat furnishing the required easily enameled "go between."

MR. LANDRUM: This may be true and would be a good explanation. There is an interaction between the iron and the enamel when you have cobalt present; when

you do not have cobalt present there is no interaction. Sample 1 (see illustration), which is enameled with the non-cobalt ground coat, is nicely covered; but under impact the enamel comes off, leaving the bright steel (see dish 3). Sample 2 is covered with the same enamel with 1 per cent. of oxide of cobalt added, and when subjected to the same blow, adheres firmly in ridges, barely exposing the steel between them (see dish 4). Samples Nos. 5 and 6 also show how the adhesiveness, under punishment by rapid changes of temperature, is promoted by the addition of oxide of cobalt. Both have been heated red hot and plunged into cold water. Number 5, whose fundamental coating contains no cobalt, peels off clean, to the steel, while 6, whose fundamental coating is the cobalt ground, exposes no steel at all.

PROF. STALEY: I would like to have Mr. Landrum prove that there is an interaction between the ground coat and the iron when cobalt is present and no interaction when cobalt is absent. I would also like to see him demonstrate the presence of a porous alloy between the enamel and iron. In regard to what Prof. Purdy has said, I would like to know on what evidence he bases his statement that cobalt is merely suspended in the ground coat and, furthermore, to explain the mechanics of just **how** such a suspension, if it should exist, would make a more tenacious ground coat. We have one fact, namely, that the addition of cobalt to a ground coat for sheet steel enamels makes it a better ground coat. This is admirably shown by Mr. Landrum's paper. Beyond this one fact, we can merely speculate **until some one produces some evidence.**

MR. LANDRUM: We are merely speculating as to the "mechanics" of the action of the cobalt, but I believe that these samples show to the naked eye that there **has** been an interaction between the steel and the cobalt-containing enamel, and that there **has not** been such an interaction in the case of the non-cobalt enamel. It might

throw light on the subject to consider the fact that even a cobalt-containing ground coat will not adhere well to a steel surface unless that surface has been made rough, or porous or crystallized by pickling, sand-blasting, or annealing. It may be that the enamel simply sinks down into the pores of the steel, but the question is: Why should an enamel have to contain cobalt to do this? Now if some one has the facilities to make a cross-section of a piece of enameled steel, I would like to see it. Such a section might explain this matter.

METHODS OF ANALYSIS FOR ENAMEL AND
ENAMEL RAW MATERIALS*

Introduction.[1] The fact that practically nothing has
been published on the above subject, and the remem-
brance of the many long hours spent in digging out these
methods and adapting them to enamels and enamel raw
materials, has led the author to put them in this form for
others who might use them. While he claims little origi-
nality in the methods themselves, he does claim originality
in the adaptations here given. Each and every one of
these methods has been thoroughly tried out, either in
the laboratory of the Columbian Enameling and Stamp-
ing Company, at Terre Haute, Ind., or in the chemical
laboratories of the University of Kansas.

PART I.

The Analysis of an Enamel

The analysis of an enamel presents one of the most
difficult and complicated problems with which the an-
alyst comes in contact. An enamel is generally an in-
soluble silicate containing besides silica, iron, alumina,
calcium, magnesium and the alkalies, generally boron,
fluorine, manganese, cobalt, antimony and tin, and some-
times phosphorus and lead. Before attempting the quan-
titative analysis of any enamel a thorough qualitative
analysis should be run, and this will enable one to choose

a quantitative separation. One of the most important aids to a correct analysis is a thorough grinding. The sample should be ground to an almost impalpable powder, and every conceivable precaution for accuracy taken.

The analysis of a sample of enamel to be taken from a piece of ware involves an extra difficulty. The coating of enamel almost always consists of two or more layers—the lower a large ground coat, and the upper ones white or colored enamels. For an illuminating analysis these must be separated. The author has found the following method of V. de Luyeres[1] good for doing this: The surface is scratched lightly with a piece of emery cloth or a file, and a coating of gum acacia or glue is applied. The vessel is placed in an air-bath and heated. The glue on hardening generally carries with it some of the outer coat. The glue or gum is then broken off, dissolved in water and the enamel pieces collected on a filter paper. Some obstinate enamels require painstaking methods, such as chipping off with a chisel and separating the different coats—which always vary somewhat in color—by picking out and sorting, using a pair of forceps. A large reading glass will be useful in making these separations. Any iron from the vessel which may adhere to the enamel may be removed by means of a magnet after the sample is ground.

Analysis of an Enamel Containing Fluorine

In an enamel containing fluorine the usual methods for silicates cannot be used, as silicon-tetra-fluoride would be volatilized in the evaporation with hydrochloric acid for the separation of the silica.

Fluorine. One gram sample is very finely ground, slowly fused with two grams each of potassium carbonate and sodium carbonate. The melt should be kept in quiet fusion over as low a flame as possible for one hour. The melt is transferred, (after cooling quickly by giving the

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[1] Compte Rendus 8, p. 480.

crucible a gyratory motion while held in the tongs, causing the melt to cling to the sides instead of forming a solid cake in the bottom), to a platinum dish where it is covered with a watch glass and boiled vigorously with one hundred cc. of water. The residue is filtered off and is saved for the determination of the metallic oxides and the silica.

The covered solution is digested on a steam bath for an hour with several grams of ammonium carbonate, and on cooling more carbonate is added and the solution is allowed to stand for twelve hours. The precipitate of silica, alumina, etc., is filtered off, washed with ammonium carbonate water and is saved for further determinations.

The solution containing all the fluorine and traces of silica, phosphate, etc., is evaporated until gummy, then diluted with water and neutralized as follows: Phenolphthalein is added, and nitric acid (double normal) drop by drop until solution is colorless.

The solution is boiled and the red color which reappears is again discharged with nitric acid, boiled again and neutralized again until one cc. of acid will discharge the color.

The last traces of silica, etc., are now removed, as recommended by F. Seemann (Zeit. Anal. Chem. 44, p. 343), by the addition of 20 cc. of Schaffgotsch solution. This solution is made as follows: 250 grams of ammonium carbonate are dissolved in 180 cc. of ammonia (0.92 sp. gr.) and the solution is made up to one liter. To the cold solution 20 grams of freshly precipitated mercuric oxide are added and the solution is vigorously shaken until the mercuric oxide is dissolved.

The precipitate caused by the Schaffgotsch solution is filtered off and saved, and the solution is evaporated to dryness and the residue taken up with water.

Any phosphorus from the bone ash used in some enamels, and chromium which may be present, are removed from this alkaline solution by adding silver nitrate in excess. Phosphate, chromate and carbonate of silver are here thrown down and may be determined if desired.

The excess of silver is removed from the solution by sodium chloride, and one cc. double normal sodium carbonate solution is added to the filtrate, and the fluorine is precipitated by boiling with a large excess of calcium-chloride solution.

The precipitate, consisting of a mixture of calcium carbonate and fluoride, is collected on a blue ribbon filter paper and is washed, dried, ignited at low red heat, separated from the filter paper, and the residue with the ash of the paper is treated with dilute acetic acid until carbon dioxide is no longer given off on heating. The liquid is then evaporated to dryness, the residue taken up with hot water (slightly acidified with acetic acid) filtered, dried and gently ignited and weighed as CaF_2. This may be checked by heating with sulfuric acid, driving off all the excess of acid and reweighing as $CaSO_4$. This method gives results for the amount of fluorine checking within 0.2%, but which are generally from 2% to 4% low.

Silica. For the estimation of silica and the metallic oxides, first the precipitate from the Schaffgotsch mercuric oxide solution is ignited to drive off the mercuric oxide, and the silica left is weighed. The residue from the original melt, together with the precipitate obtained by ammonium carbonate (after the drying and removal from the filter paper whose ash is added) are then dissolved in hydrochloric acid. The solution is evaporated to dryness and moistened with hydrochloric acid. It is diluted with water and the silica is filtered off, weighed, and this with that previously obtained is the total silica.

Iron, Alumina and Manganese. The solution from the silica is raised to boiling and the iron and aluminum

are precipitated as hydroxides. Then 5 cc. of bromine water is added and the boiling continued for five minutes. The precipitate is dried on filter-paper and ignited separately from it in a weighed platinum crucible, to which the ash of the filter-paper is afterwards added. The precipitate consists of Al_2O_3, Fe_2O_3, and Mn_2O_3, and is weighed as such. It is then fused with fifteen times its weight of potassium pyrosulfate over a low flame for three hours with the crucible covered. The crucible, contents and cover are placed in a beaker and dilute sulfuric acid (10:1) is added. By warming and continued shaking of liquid complete solution may be obtained. It is then drawn through a Jones Reductor to change all the iron to ferrous and titrated with N/10 potassium permanganate solution. The iron is calculated to Fe_2O_3 and the alumina determined by difference.

If manganese is present it is determined in a separate sample in a method given later and is subtracted from the iron in the above. In white enamels containing only a trace of iron the manganese may be determined in the solution from the pyrosulfate fusion. A freshly prepared solution of potassium ferrocyanide is added to oxidize the manganese, then the solution is made alkaline with sodium hydroxide solution and the manganese-dioxide thus formed is filtered off. The solution is then made acid and the ferrocyanide is titrated with N/10 potassium permanganate solution. (1 cc. $KMnO_4 = 0.00435$ gram MnO.)

Calcium Oxide. The filtrate from the iron and alumina is raised to boiling, treated with boiling ammonium oxalate solution and digested on water bath until precipitate readily and quickly settles after being stirred. The calcium oxalate is now filtered off and ignited wet in platinum to constant weight over a strong blast.

Magnesium Oxide. The solution is evaporated to dryness and the residue ignited to remove ammonium salts. The residue is treated with a few drops of hydro-

chloric acid and taken up with boiling water and filtered from the carbonaceous residue. To the boiling solution is added drop by drop a solution of sodium ammonium phosphate and is allowed to cool. Half as much concentrated ammonium hydroxide is added as there is solution and it is allowed to stand over night. The precipitate is collected on a filter, washed with 3% ammonia water, dried in oven and ignited separate from the filter. The heat is applied gently at first and finally with the highest heat of a good Bunsen burner. It is then weighed as $Mg_2P_2O_7$.

$$1 \text{ gram } Mg_2P_2O_7 = .3625 \text{ grams } MgO$$

The alkalies are determined by the method of J. Lawrence Smith from a gram sample finely powdered. This method is standard and need not be given here.

Separation and Determination of Antimony, Tin, Manganese and Cobalt in Enamel

Decomposition. Two grams finely powdered sample are transferred to a platinum dish, and after moistening with a little water, pure hydrofluoric acid is added and the whole is mixed with a platinum spatula. The dish is digested on steam bath for five hours covered with platinum cover (a larger platinum dish may be used for cover if no other is at hand). After the decomposition is complete the solution is evaporated to dryness on steam bath. The residue is moistened with enough dilute sulfuric acid (1:1) to make a thin paste, and evaporated as far as possible on a steam bath and then on a hot plate, all the time being covered to prevent spirting. As soon as fumes of sulfuric anhydride cease to be evolved the cover is strongly heated until fumes cease to be driven off, when it is removed. The contents are heated by bringing the dish to dull redness directly over a Bunsen burner. The sulfates thus formed are moistened with strong hydrochloric acid, a little hot water is added and the solution boiled with repeated additions of acid and water until

completely in solution. In some enamels—especially those with high melting points—the stannic oxide remains undissolved, and a fusion of the residue with sulfur and sodium carbonate as given later under "The Analysis of Oxide of Tin" may be necessary.

Treatment with H₂S. The solution containing at least 30 cc. double normal hydrochloric acid is transferred to a 500 cc. Ehrlenmeyer flask fitted with a double bored stopper. Through one of the holes a right-angled piece of glass tubing is introduced that just reaches to the lower edge of the stopper, while through another hole another right-angled glass tube is fixed so that it almost reaches the bottom of the flask.

A Kipp H_2S generator is connected to the longer tube and H_2S is passed through for half an hour and the solution is let stand for another half an hour, after which the sulfides of antimony and tin are transferred to a filter paper and the solution is kept for the determination of manganese and cobalt.

Antimony and Tin. The precipitated sulfides are dissolved in a solution of potassium polysulfide—if any lead or copper is present it will remain undissolved and may be determined separately—by pouring this successively through the filter into a 300 cc. Jena beaker, and finally washing with water containing a small amount of potassium polysulfide.

Antimony. The antimony and tin in this solution are separated by F. W. Clark's method as modified by F. Henz[1], as follows:

To the solution in the Jena beaker 6 grams caustic potash and 3 grams tartaric acid are added. To this mixture twice as much 30 per cent. hydrogen peroxide is added as is necessary to completely decolorize the solution, and the latter is now heated to boiling and kept there

[1] Treadwell, Vol. II, p. 188.

until the evolution of oxygen is over, in order to oxidize the thiosulphate formed. All of the excess of peroxide cannot be removed successfully at this point. The solution is cooled somewhat, the beaker covered with a watch-glass, and a hot solution of 15 grams pure recrystallized oxalic acid is cautiously added (5 gms. for 0.1 gm. of the mixed metals). This causes the evolution of considerable carbon dioxide. Now, in order to completely remove the excess of hydrogen peroxide the solution is boiled vigor-ously for ten minutes. The volume of the liquid should amount to from 80 to 100 cc. After this a rapid stream of hydrogen sulfide is conducted into the boiling solution, and for some time there will be no precipitation, but only a white turbidity formed. At the end of five or ten min-utes the solution becomes orange colored and the anti-mony begins to precipitate, and from this point the time is taken. At the end of fifteen minutes the solution is di-luted with hot water to a volume of 250 cc., at the end of another fifteen minutes the flame is removed, and ten minutes later the current of hydrogen sulfide is stopped. The precipitated antimony pentasulfide is filtered off through a Gooch crucible which, before weighing and after drying, has been heated in a stream of carbon di-oxide at 300° C. for at least one hour. The precipitate is washed twice by decantation with 1 per cent. oxalic acid and twice with very dilute acetic acid before bring-ing it in the crucible. Both of these wash liquids should be boiling hot and saturated with hydrogen sulfide.

The crucible is heated in a current of carbon dioxide (free from air) to constant weight, and its contents weighed as Sb_2S_3.

The filtrate is evaporated to a volume of about 225 cc., transferred to a weighed unpolished platinum dish, and electrolyzed at 60° to 80° C. with a current of 0.2 to 0.3 ampere (corresponding to 2 to 3 volts). For very small amounts of tin, a current of not over 0.2 ampere should be used. At the end of six hours 8 cc. of sulfuric

acid (1:1) are added, and at the end of twenty-four hours the solution is transferred to another dish. The deposited tin has a beautiful appearance, similar to silver.

Tin. The plated tin is washed thoroughly with water and the dish is dried in an air oven at 110° and weighed.

The solution containing the cobalt and manganese is boiled until free from H_2S. The iron is oxidized back to the ferric state by the addition of bromine water and boiling until the excess of the latter is expelled. Ten cc. double normal ammonium chloride is added and the iron and alumina are precipitated by the addition of ammonia and are filtered off. (The iron alumina may be determined from this precipitate if desired.)

The solution still containing the manganese and cobalt is transferred to an Ehrlenmeyer flask fitted for passing in H_2S, as before described, and 3 cc. strong ammonia is added. H_2S is passed through for some time, and after precipitation ceases 3 cc. more of ammonia are added and the flask is filled to the neck (300 cc. flask), is corked and set aside for twelve hours at least. The precipitate is collected and washed on a small filter with water containing ammonium chloride and sulfide.

Manganese. The manganese is extracted from the precipitate on the filter by pouring through it strong H_2S water acidified with 1-5 its volume hydrochloric acid (sp. gr. 1.11). This solution from the extraction is evaporated to dryness, ammonium salts are destroyed by evaporation with a few drops of sodium carbonate solution, hydrochloric acid and a drop of sulfurous acid are added to decompose excess of carbonate and to dissolve the precipitated manganese, and the latter is reprecipitated at boiling heat by sodium carbonate after evaporating off the hydrochloric acid. The manganese is weighed as Mn_3O_4 and calculated to MnO_2, in which form it is probably present in the enamel.

The residue of cobalt sulfide left after extracting the manganese is burned in a porcelain crucible, dissolved in

aqua regia, and evaporated with hydrochloric acid; the platinum—and copper if any is present—are thrown down by heating and passing in hydrogen sulfide. The filtrate from the platinum and copper is made ammoniacal, and cobalt is thrown down by hydrogen sulfide. This is filtered off and washed with water containing ammonium sulfide. This is either ignited and weighed as oxide or more accurately determined by dissolving in an ammoniacal solution of ammonium sulfate, containing 10 grams of ammonium sulfate and 40 cc. of concentrated ammonia for each 0.3 grams of cobalt, and electrolyzing in a weighed platinum dish at room temperature with a current of 0.5 to 1.5 ampere, and an electromotive force of 2.8 to 3.3 volts. The electrolysis is finished in three hours. The circuit is broken and the liquid poured off, and the platinum dish is washed with water, then with absolute alcohol (distilled one hour) and finally with ether, allowed to dry in oven at 95° for one minute and then weighed. The metallic cobalt is calculated as CoO, in which form it is present in the enamel.

The Determination of Boric Anhydride in Enamel

The boron is determined in a separate sample of about 0.3 grams. This finely pulverized sample is fused with three grams sodium carbonate for fifteen minutes, is taken up with thirty cc. dilute hydrochloric acid and a few drops of nitric acid. The melt is heated in a 250 cc. round-bottomed flask almost to boiling, and dry precipitated calcium carbonate is added in moderate excess. The solution is boiled in the flask after it has been connected with a six-inch worm reflux condenser. The precipitate is filtered on an 8 cm. Buchner[1] funnel, and is washed several times with hot water, taking care that the total volume of the liquid does not exceed 100 cc.

The filtrate is returned to the flask, a pinch of calcium carbonate is added and the solution is heated to

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[1] See Method of Wherry and Chapin, Jr., Am. Chem. Soc. 30, p. 1688, for Determination of Boron in Silicates.

boiling to remove the free carbon dioxide. This is best done by connecting the flask to a suction pump, and the suction is applied during boiling. The solution is cooled to ordinary temperature, filtered if the precipitate has a red color, and four or five drops of phenolphthalein is added and N/10 sodium hydroxide solution is run in slowly until liquid has a strongly pink color. A gram of mannite (or 150 cc. of neutral glycerol) is added, whereupon the pink color will disappear. Continue to run in N/10 sodium hydroxide until end point is reached. Add more mannite or glycerol and if necessary more alkali, until a permanent pink color is obtained.

<div align="center">1 cc. N/10 Sodium Hydroxide = .0035 g. B_2O_3</div>

Lead. The enamel for cooking utensils should never contain lead. To determine whether a cooking utensil contains lead, E. Adam gives the following simple qualitative method: A small piece of filter paper moistened with hydrofluoric acid is placed upon the enamel and allowed to remain for some minutes; the paper, together with any pasty mass adhering to the enamel, is then washed off into a small platinum basin, diluted with water, and tested for lead by passing H_2S through the solution.

J. Grunwald (Oesterr. Chem. Ztg. 8, p. 46) gives another quick test for lead: Wet small portion of surface with HNO_3 (conc.) and heat until acid is evaporated. Add several drops of water and a few drops 10% potassium iodide solution, and if even a trace of lead is present yellow lead-iodide will be produced.

Determination of Phosphoric Anhydride in Enamel

Enamels containing bone ash to give opaqueness are analyzed for P_2O_5 as follows:

To a gram sample of very finely pulverized enamel in a platinum crucible one cc. of sulfuric acid is added and the crucible is filled half full (about ten cc. are re-

quired) with hydrofluoric acid. The crucible is heated on the water bath until most of the solution is evaporated and then gently on a hot plate to remove all the fluorine as silicon-tetra-fluoride and as hydrofluoric acid, but no sulfuric acid fumes should evolve, as P_2O_5 is volatile. The residue is dissolved in nitric acid and taken to dryness, moistened with nitric acid, diluted with water, filtered and washed with a very little water.

Add aqueous ammonia to the solution from above until the precipitate of calcium phosphate first produced just fails to redissolve, and then dissolve this by adding a few drops of nitric acid. Warm the solution to about 70° C. and add 50 cc. ammonium molybdate solution (70g. MoO_3 per liter). Allow the mixture to digest at 50° for twelve hours. Filter off precipitate washing by decantation with a solution of ammonium nitrate made acid with nitric acid.

The precipitate on the filter is dissolved by pouring through it dilute ammonia solution (one volume of 0.96 sp. gr. ammonia to three volumes of water).

The solution is received in the beaker containing the bulk of the precipitate, all of which is dissolved in the ammonia solution.

An excess of magnesium ammonium chloride ("magnesia mixture") solution is added very slowly and with constant stirring. Let solution stand over night. Decant clear solution through a filter and wash by decantation with ammonia water (1:3). Dissolve the precipitate by pouring a little hydrochloric acid (sp. gr. 1.12) through the filter, allowing the acid solution to run into the beaker containing most of the precipitate. When all the precipitate on the filter and in the beaker is dissolved wash the filter paper with a little hot water. To the solution add 2 cc. magnesia mixture and then strong ammonia, drop by drop, with constant stirring until distinctly ammoniacal. Stir several minutes, then add strong ammonia equal to one-third of the liquid, let stand two hours and filter off

the precipitate of magnesium ammonium phosphate. Wash with dilute ammonia water, dry the precipitate, ignite separately from the filter, first at low temperature and gradually raise to full blast. Weigh precipitate as $Mg_2P_2O_7$ and calculate as P_2O_5 in sample.

PART II.

THE ANALYSIS OF ENAMEL RAW MATERIALS

The Analysis of Borax

Sampling. A handful is taken from the middle of every tenth bag as it is unloaded. The sample from the entire car-load is then quartered down to two pounds. This is crushed so that it will pass through a forty mesh sieve. This is futher quartered to about thirty grams. Sample is then accurately weighed and thoroughly dissolved in about 600 cc. hot—not boiling—water in a liter volumetric flask, and when cool is diluted to the mark. One hundred cc. of this, representing one-tenth of the sample, is then taken for analysis.

Determination of Sodium Oxide and Boric Acid. Titrate with normal sulfuric or hydrochloric acid solution, using methyl orange as indicator.

Number cubic centimeters Normal Acid $\times$ .031 $=$ g, Na_2O. The solution is now boiled, covered with a watch glass to expel CO_2, and on cooling may turn pink. Add normal KOH solution (a drop will do) to bring back yellow color. At this stage all the boric acid exists in a free state.

$(2Na^+ + B_4O_7^{--}) + H_2O + (2H^+ + 2Cl^-) = (2Na^+ + 2Cl^-) + 4(H^+ + 4BO_2^-)$
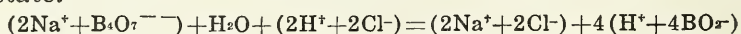
Add as much neutral glycerol as there is solution (about 150 cc.) and titrate with normal potassium hydroxide, using phenolphthalein as indicator. If end is not distinct add more glycerol and more indicator. The addition of glycerol causes the boric acid to become more

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dissociated, probably due to the formation of boroglyceric acid, and the end-point is quite distinct. The following equation represents essentially what takes place:

$$(4H^+ + 4BO_2^-) + (4K^+ + 4OH^-) = (4K^+ + 4BO_2^-) + 4H_2O$$
$$1 \text{ cc. normal KOH solution} = .035 \text{ g. } B_2O_3$$
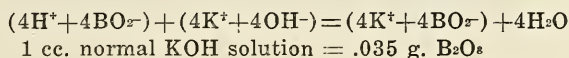
If the analysis gives more Na_2O than is required to calculate all the B_2O_3 to $Na_2B_4O_7$, the remainder comes from sodium carbonate with which it has been adulterated.

Calculation of Results. The analysis of the borax is very important, as many times samples are adulterated, and even when not adulterated seldom contain exactly enough water to give the formula $Na_2B_4O_7 \cdot 10H_2O$. It is necessary to know the strength of the borax not only to buy intelligently, but also so that each and every mix of enamel will contain the same amount of borax.

It is customary to calculate from the percent of B_2O_3 in sample the percent strength of the sample as $Na_2B_4O_7 \cdot 10H_2O$.

$$\%B_2O_3 \times 2.7307 = \%Na_2B_4O_7 \cdot 10H_2O$$

When the sample has dehydrated of course this will run over 100%, and thus the correspondingly fewer pounds of borax may be used in the mix of enamel.

Moisture. On account of the large amount of water of crystallization in borax it is difficult to determine the moisture directly, therefore it is calculated by subtracting the % $Na_2B_4O_7 \cdot 10H_2O$ and the % Na_2CO_3 (if any is present) from 100%.

The Analysis of Ground Sand, Flint and Quartz

Fineness. These, as are most of the raw materials used in the enamel, are tested for fineness. One kilogram is weighed on balance sensitive to 1/10 gram and is shaken on a 100 mesh sieve. The material remaining on

the sieve is weighed. This is then shaken on an 80 mesh sieve and the residue weighed. From this is calculated percent through 100 mesh and percent through 80 mesh. The finer the material the better it is for use in making enamel.

An analysis for SiO_2, Fe_2O_3 and MgO is run when a new material is being tried, but generally only the SiO_2 and Fe_2O_3 are determined. In this case the acid solution from the silica is reduced by passing through a Jones Reductor and is titrated with $N/10$ potassium bichromate.

Preparation for Analysis. The material is carefully sampled by quartering down to several grams. This is ground in an agate mortar to pass completely through a hundred mesh sieve. This grinding is generally done by hand but an enameling works laboratory should be equipped with a McKenna Grinder, (manufactured by McKenna Bros. Brass Company, Ltd., of Pittsburgh), in which the material can be ground in an agate mortar by power.

The method followed for the analysis of flint and other forms of silica as well as clays and feldspars, is in all essentials, a well known method given by Hillebrand in analysis of silicate rocks, U. S. Geological Survey Bull. 305, and for reasons of space this method will not be given here.

The Determination of Titanium in Enamels, Clays and Silicate Minerals

Titanium is determined after the determination of the iron by titrating with permanganate. This solution (after titrating) is diluted to 1000 cc. and is treated with hydrogen peroxide and the titanium determined by A. Weller's Colorimetric Method,[1] from one-half the solution.

This determination depends upon the fact that acid solutions of titanium sulphate are colored intensely yel-

[1] Berichte 15, p. 25-93.

low when treated with hydrogen peroxide; the yellow color increases with the amount of titanium present and is not altered by an excess of hydrogen peroxide. On the other hand, inaccurate results are obtained in the presence of hydro-fluoric acid (Hillebrand); consequently it is not permissible to use hydrogen peroxide for this determination which has been prepared from barium peroxide by means of hydrofluosilicic acid. Furthermore, chromic, vanadic, and molybdic acids must not be present, since they also give colorations with hydrogen peroxide. The presence of small amounts of iron do not affect the reaction, but large amounts of iron cause trouble on account of the color of the iron solution. If, however, phosphoric acid is added to the colored ferric solution it becomes decolorized, and from such a solution the determination of titanium offers no difficulty. The solution in which the titanium is to be determined must contain at least 5 per cent. of sulfuric acid; an excess does not influence the reaction. The reaction is so delicate that 0.00005 gm. of TiO_2 present as sulphate in 50 cc. of solution give a distinctly visible yellow coloration.

For this determination a standard solution of titanium sulfate is required. This can be prepared by taking 0.6000 gm. of potassium titanic fluoride which has been several times recrystallized and gently ignited (corresponding to 0.2 gm. of TiO_2). This is treated in a platinum crucible several times with a little water and concentrated sulfuric acid, expelling the excess of acid by gentle ignition, finally dissolving in a little concentrated sulfuric acid and diluting with 5 per cent. sulfuric acid to 100 cc. One cubic centimeter of this solution corresponds to 0.002 gm. TiO_2.

The determination proper is carried out in the same way as the colorimetric determination of ammonium in the sanitary analysis of water.

50 cc. of the solution which has been brought to a definite and accurately measured volume is placed in a

Nessler tube beside a series of other tubes, each containing a known amount of the standard titanium solution, filled up to the mark with water and each treated with 2 cc. of 3 per cent. hydrogen peroxide[1] (free from hydrofluoric acid). The color of the solution in question is compared with the standards. This method is only suitable for the estimation of small amounts of titanium, as the shades of strongly colored solutions cannot be compared accurately.

The Analysis of Oxide of Tin

Stannic Oxide. As this is one of the most important and most expensive of the raw materials used in enameling, an analysis is very necessary. The oxide is bought to contain not less than 99.5% SnO_2, and in this the impurities will consist of minute traces only of other materials. For an oxide of this kind from .2 to .3 of a gram of the sample is placed in a porcelain casserole, about 10 cc. of C. P. nitric acid of a sp. gr. 1.2 is added and the solution is slowly evaporated to a volume of about 2 or 3 cc., diluted to about 30 or 40 cc. of water, kept warm for about a half hour, filtered on a small blue-ribbon filter paper, and washed with warm water, slightly acidulated with nitric acid, being careful to avoid letting the precipitate creep up.

The precipitate is dried on filter paper in the funnel by placing in a hot air bath. The dried tin oxide is then removed as completely as possible from the filter paper and the paper is ignited in a porcelain crucible, being sure that there is an excess of air so that there will be no metallic tin reduced.

The balance of oxide of tin is now added to the crucible and the whole is moistened with a drop of nitric acid, the temperature under the crucible is gradually raised until it comes to a bright red heat over the blast flame.

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[1] The hydrogen peroxide solution is prepared shortly before using by dissolving commercial potassium percarbonate in dilute sulfuric acid.

This method gives results which check within one-tenth of a per cent.

Some brands of oxide of tin on the market contain a number of impurities in considerable quantities. Lead, iron, silica, Sodium chloride, sodium sulfate and water are the most common of these. These are determined as follows:

Direct Method. Methods for the direct determination of the tin have proven quite unsatisfactory but the following, with very careful manipulation, yields results checking within 0.2%:

Five-tenths grams of oxide is mixed in a porcelain crucible with 3 grams each of powdered sulfur and dry carbonate of soda, which both of course must be C. P., especially free of metals and earths. The covered crucible is heated for about an hour at **low heat first,** and later at the heat of a regular Bunsen burner; then let cool without lifting the cover. The cold mass is dissolved in water, filtered and washed with water to which was added a little sulfide of ammonia; the residue is brought back in the crucible and the melting process repeated, of which the solution is filtered to the first melting. The sulfide tin solution then is acidulated with hydrochloric acid and the precipitated sulfide of tin is allowed to settle clearly, after which it is filtered and washed with sulfide of hydrogen water.

The wet precipitate of sulfide of tin is transferred to an Ehrlenmeyer flask and treated with dilute hydrochloric acid and bromine until completely dissolved, at a low heat. The filter left after the solution is filtered off is washed and the $SnCl_2$ solution is precipitated with ammonia and a little nitrate of ammonia, allowed to settle, filtered and washed. After drying, the precipitate is ignited at white heat and is weighed as SnO_2.

Reduction Method. When the qualitative analysis shows no metal other than tin present, a very satisfactory

method is to reduce a weighed quantity of the sample in a Rose crucible by heating to redness in a stream of hydrogen. The silica, if any is present, may be determined by dissolving out the tin with hydrochloric acid and weighing the residue.

Combined Water. In oxides which are prepared by certain precipitation methods, the combined water runs as high as ten per cent. To determine this, a two gram sample is heated in a porcelain crucible at a white heat to constant weight. The loss is combined water.

Lead. The lead is determined from the nitric acid solution and washings from the tin oxide determination by precipitation as the sulfate.

Iron. Digest about one gram with twenty-five cc. of concentrated hydrochloric acid. As much water is added and the solution is boiled for five minutes. The residue is filtered off and about a cubic centimeter of concentrated sulfuric acid is added and the solution is evaporated until the sulfuric fumes come off. The solution is diluted, passed through a Jones Reductor and titrated with N/10 potassium permanganate solution.

Soluble Salts. About two grams of the sample is boiled with water for thirty minutes. The residue is filtered on a blue-ribbon paper and is dried in an air bath. It is then separated as completely from the paper as is possible. The paper is burned in a platinum crucible. A drop of nitric acid is added and the crucible is raised to bright red. The whole of the residue is now added and heated to white heat for some time. (If there was combined water present in the sample of course it will be driven off, and this must be taken into calculation).

The loss in weight (minus the above correction) is the soluble salts—usually sodium chloride and sulfate.

If desired these may be determined definitely by usual methods. (Titration of an aliquot part with N/10 silver nitrate solution for the chloride and precipitation of

the sulfate as barium sulfate in another aliquot part slightly acidifies with nitric acid.)

Silica. To the residue in the platinum crucible from the above determination several drops of sulfuric acid are added, and the crucible is filled within a quarter of an inch of the rim with pure hydrofluoric acid. This is volatilized, carrying with it any of the silica as hydrofluosilicic acid. Loss of weight = SiO_2.

The Analysis of Pyrolusite

Pyrolusite has two uses in enamel, first as an oxidizing agent, and second to give an amethyst color to the enamel frit. Its grading, however, is generally made on its oxidizing value. This is found as follows:

Manganese Dioxide. A sample is carefully taken from each barrel of the shipment, and after quartering down to about ten grams is ground so as to pass through a 200 mesh sieve. (It is better to test this by seeing if any grit can be detected when the powder is placed between the teeth.) The sample is dried, spread out on a watch glass, at 110° for one hour, transferred to a stoppered weighing tube, and after weighing, about one-half gram is transferred into a 250 cc. Ehrlenmeyer flask. For each gram of sample weighed out add at least 0.9 grams **pure,** tested oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) weighing the acid accurately and recording the same. Add about 30 cc. of water and 30 cc. 5 normal sulfuric acid and drive off carbon dioxide by heating gently.

It is seldom necessary to filter after some practice, so the solution is titrated hot for the excess of oxalic acid with N/10 potassium permanganate solution. Calculate amount of oxalic acid oxidized by the pyrolusite. The reaction is

$$MnO_2 + H_2C_2O_4 \cdot 2H_2O + H_2SO_4 = MnSO_4 + 2CO_2 + 4H_2O$$
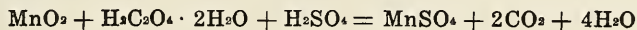
Each gram oxalic acid oxidized therefore corresponds to .6902 g. MnO_2.

As pyrolusite is added to some enamels only to give color it is sometimes necessary to know its coloring power, and this is dependent upon the total manganese.

Total Manganese. One-half gram sample is boiled with strong hydrochloric acid until chlorine ceases to be evolved. The solution is neutralized with calcium carbonate and an excess of a strong filtered solution of bleaching powder is added. The solution is boiled until deep red, then alcohol is added until the red color disappears. The whole of the manganese now exists as MnO_2 and may be reduced with oxalic acid and titrated for its oxidizing power as before with N/10 permanganate of potassium. Each gram of oxalic acid oxidized corresponds to .4361 g. Mn.

The Analysis of Soda Ash and Pearl Ash

Generally it is only necessary to determine the total alkali in a sample of either soda ash or pearl ash, and to calculate from this the percentage of Na_2O or K_2O. A more complete analysis includes the determination of insoluble matter, iron, chloride, sulfate and moisture, as well as the total alkali.

Insoluble Matter. 50 g. weighed on rough balance (sensitive to 0.1 g.) and sufficient water added to dissolve the ash, shaking until dissolved. After an hour's digestion the solution is filtered through a weighed Gooch crucible with a circle of filter paper covering the bottom. This is dried at 105° and the increase in weight is insoluble matter.

Iron. The iron in the above insoluble matter is dissolved by pouring hot dilute hydrochloric acid through the precipitate in the Gooch crucible. The iron is precipitated from this by ammonium hydroxide and filtered on a white ribbon filter paper. The still moist precipitate is dissolved in sulfuric acid, reduced by means of a Jones Reductor and titrated with N/10 permanganate.

90

Chloride. Three gram samples are dissolved in water and nitric acid added until the solution is neutral (test with litmus paper). It is then titrated with N/10 silver nitrate solution.

Sulfate. Five or ten grams are dissolved in hydrochloric acid and the sulfate precipitated from the almost boiling solution by the addition of hot barium chloride solution.

Total Alkali. Twenty-five grams are dissolved in water in a 500 cc. volumetric flask and 50 cc. are titrated with N. hydrochloric acid, using methyl orange as indicator.

Hydroxide. To 50 cc. from above, precipitate all the carbonate with barium chloride. Without filtering, add phenolphthalein and titrate until colorless with normal hydrochloric acid.

Moisture. Ten gram samples are dried at 120° for two hours.

The Analysis of Saltpeter and Chili Saltpeter

Moisture. Ten gram samples are heated to constant weight in an air-bath at 130°.

Insoluble Matter. Twenty grams are dissolved in boiling water and filtered through a weighed Gooch crucible with a circle of filter paper on the bottom. After drying at 110° in air bath to constant weight, the increase in weight is the insoluble matter.

Chlorine. The solution from above—this should be about 500 cc.—is placed in a 1000 cc. volumetric flask and 25 cc. (representing 0.5 g. sample) is titrated with N/10 silver nitrate, using potassium chromate as indicator. The result is calculated to sodium chloride.

Sulfate. Twenty cc. are heated to boiling and precipitated by adding hot barium chloride solution, a drop at

a time and with constant stirring. After two hours digestion (or until precipitate settles quickly after agitating), filter through a Gooch crucible with ignited asbestos filter, ignite and weigh as barium sulfate. This is calculated to calcium sulfate.

Calcium and Magnesium. From five hundred cc. of the above solution (equal to 10 grams sample) at boiling temperature precipitate the calcium as oxalate by the addition of ammonium oxalate, being careful not to add much excess, as magnesium is to be determined in the same sample. Filter on a white ribbon filter paper, after an hour's digestion on the steam bath, ignite wet paper in platinum crucible, gradually increase to full blast and heat to white heat to constant weight. Weight as calcium oxide.

Determine the magnesium in filtrate from the calcium by addition of a solution of microcosmic salt and afterward one-third the volume of concentrated ammonium hydroxide, added drop by drop. The precipitate, ignited separate from the filter paper, is heated at first gently and at last with the full heat of a Bunsen burner, and weighed as magnesium pyrophosphate ($Mg_2P_2O_7$).

Perchlorate. Ten grams of the sample of which the chloride content has already been determined, is mixed with an equal quantity of chemically pure sodium carbonate, and is heated in a large, covered platinum crucible to quiet fusion. Ten or fifteen minutes are required. The product is then dissolved in nitric acid and the chloride estimated as usual.

Nitrogen. This is determined by the Kjeldahl method after reducing the nitrate to ammonia. Twenty grams of the sample are ground coarsely and dissolved in water in a liter flask, and solution is diluted to the mark. Twenty-five cc. (equal to 0.5 g. sample) of this solution is mixed in a 800 cc. Kjeldahl flask with 15 cc. concentrated

sulfuric acid to which 2 grams salicylic acid have been added, then add gradually 2 grams zinc dust and shake flask to mix contents. Digest over low flame with neck of flask slightly inclined until danger of frothing has passed. Increase flame until the acid boils briskly and until white fumes cease to come off. This usually takes about ten minutes.

Add .7 gram mercuric oxide and continue boiling, adding acid if necessary to keep solution from solidifying. Solution should be clear in a short time. Complete oxidation by adding a little powdered potassium permanganate and allow the contents to cool. Add about 200 cc. ammonia-free water and 25 cc. potassium sulfide solution (40 g. commercial salt to the liter) and shake thoroughly. Add several pieces of granulated zinc and then pour carefully down the side of the neck 100 cc. sodium hydroxide solution (500 g. per liter), avoiding shaking and thereby mixing the acid and alkali. After washing the neck with ammonia-free water connect the flask immediately with a previously set up block tin condenser, which has been thoroughly washed and the tips of whose delivery are immersed in 30 cc. standard acid solution (half normal), colored with methyl orange contained in a 150 cc. Phillip's flask. Mix contents of digestion flask by shaking thoroughly, then heat carefully, then slowly (taking about an hour) distill over 200 cc. of the liquid. Titrate excess of acid with standard half normal alkali solution, and from this calculate percentage of nitrogen in sample.

Lung Nitrometer Method. Where frequent analyses are made the Lung[1] Nitrometer method is better. A nitrometer modified especially for the use of the determination of nitrate in saltpeter is here illustrated. The Nitrometer "A" and the leveling tube "B" are filled with mercury. From a twenty gram sample which has been dried at 110° to constant weight as nearly as is possible 0.35 grams is put into a weighing tube. This is then accurately weighed

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[1] Berichte 1885, 18, 1391.

and the contents shaken into the entry tube "C." The weighing tube is again weighed and the difference in weight is the grams sample employed. This should be close to 0.35 grams so that the gas evolved will be more than 100 cc. and less than 130 cc. at ordinary temperature and pressure.

About .5 cc. water is then poured in and the solution and crystals (after a minute's standing) are drawn into the measuring tube by opening the three-way cock into the entry tube "C" and lowering the leveling bulb cautiously. The cup is washed, using less than 1 cc. of water, and about 15 cc. of strong sulfuric acid is admitted through the entry tube into the measuring tube. (More than 1½ cc. H_2O renders the acid too dilute and the mercury is attacked). After the cock is closed the leveling tube is placed in a clamp, the measuring tube is thoroughly shaken and the following reaction takes place:

$$MnO_2 + H_2C_2O_4 : 2H_2O + H_2SO_4 = MnSO_4 + 2CO_2 + 4H_2O$$
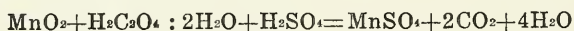
The measuring tube is now placed in clamp on a level with the levelling tube and solution is allowed to cool for an hour.

The tube is then accurately leveled, allowing one division of mercury for each six and one-half divisions of acid, and the gas volume read off. The temperature and barometric pressure are read and the gas corrected to standard conditions. Each cc. NO gas corresponds to .0037986 g. $NaNO_3$ or .003845 g. KNO_3.

The Analysis of Cryolite

Cryolite is a mineral occurring in large quantities in Greenland, and is the sodium salt of hydrofluo-aluminic acid, Na_3AlF_6. It is used in enamels and is fused, finely ground with the frit giving it a milky opaqueness which enamellers call "body." It is a very expensive material and is most always far from pure, either being deliberately adulterated or merely naturally impure.

Methods used by most chemists for its analysis are at the best crude. The direct determination of the fluorine is the only satisfactory means of properly grading it. The method used for cryolite is exactly the same as that employed in the analysis of fluorine-bearing enamel as given in the beginning of this article, except that one gram of the cryolite is finely ground with about three grams (accurately weighed) of pure silica, and this mixture is fused with about eight grams of equal parts of sodium carbonate and potassium carbonate. In determining the silica in the cryolite, this silica which has been added must be deducted from that found.

The alkalies are determined by the method of J. Lawrence Smith[1] from a gram sample finely powdered.

Combination of Results. All soda is combined with sufficient fluorine to form sodium fluoride (NaF_2). The remainder of the fluorine is combined with aluminum as aluminum fluoride (AlF_3). The remainder of the aluminum is calculated as alumina (Al_2O_3).

The Analysis of Fluorspar

Fluorspar is analyzed especially for the fluorine content by the same method as that given under Cryolite. It is a material seldom adulterated and a mere fusion with six times the weight of sodium carbonate, the taking to dryness with hydrochloric acid as in ordinary silicate analysis, the removal of iron and alumina as hydroxide with ammonia, and the precipitation with ammonium oxalate of the calcium and its final weighing as calcium oxide, is sufficient in most cases. All the calcium may be calculated as CaF_2. The determination of the fluorine, however, is of course the only exact method of accurately grading this material.

The approximate method for determining the fluorine is as follows:

Approximate Method for Fluorine. About one gram of sample finely ground and accurately weighed is in-

[1] Am. Jour. Science (2) 50, p. 269. Treadwell-Hall Anal. Chem., Vol. II, p. 394.

timately mixed in agate mortar with about the same quantity of pure silica. The whole is transferred to a 250 cc. Ehrlenmeyer flask—rinsing the mortar with more silica The flask is weighed and a weighed quantity of concentrated sulfuric acid is added. The record should now show the weight of flask, silica and acid. The flask is gently heated and the loss of weight is calculated as silicon fluoride.

Iron. For use in light colored enamels the iron content of the fluorspar is important. Five grams, finely ground, are heated in a platinum dish with an excess of sulfuric acid as long as hydrofluoric acid is given off.

After cooling it is diluted with 100 cc. of water, and after reducing by drawing through a Jones Reductor the solution is titrated with N/10 potassium permanganate solution.

Accurate Method for Fluorine. The fluorine may be accurately determined by the following method:

One gram sample (ground to pass through 200 mesh sieve) is mixed with three grams silica and three grams each sodium carbonate and potassium carbonate in a platinum crucible. **Heat gradually** until it is in quiet fusion. The thin liquid fusion soon changes to a thick paste or only sinters somewhat. The reaction is complete when there is no further evolution of carbon dioxide.

After fusion the melt is treated with water and after cooling the insoluble residue is filtered off and thoroughly washed. The solution contains all fluorine and considerable silica. Remove the silica by adding four grams solid ammonium carbonate. Heat liquid at 40°C. for some time and let stand over night. Filter in morning and wash with ammonium carbonate water.

Evaporate on water bath almost to dryness in platinum dish (keep covered, as liquid foams). Dilute with a little water. Add a few drops of phenolphthalein. Add

dilute HCl until colorless. Heat on steam bath and color will return. Cool and repeat operation until 1.5 cc. double normal HCl is sufficient to make colorless. Remove last traces silica by treating the solution with a solution of moist zinc oxide in ammonia water. Boil until ammonia is completely expelled. Filter off silica and zinc oxide and wash with water.

Precipitate fluorine as calcium fluoride and calcium carbonate by adding an excess of calcium chloride. Filter, using blue ribbon paper, and wash thoroughly with hot water. Dry precipitate on funnel. Transfer as much as possible to a platinum crucible. Burn filter and add ash. Ignite contents of crucible.

After cooling the mass is covered with a slight excess of dilute acetic acid (this changes the calcium oxide to soluble acetate). Evaporate to dryness on steam bath. Take up with water. Filter, wash and dry. Transfer most of precipitate to weighed platinum crucible. Burn filter paper. Add ash. Ignite and weigh as calcium fluoride CaF_2. To confirm the results add cautiously little concentrated sulfuric acid. Evaporate off excess sulfuric acid, ignite and weigh as calcium sulfate.

The Analysis of Oxides of Antimony

Arsenic. One gram of oxide of antimony is dissolved in 10 cc. of strong hydrochloric acid—at as low a temperature as possible. The solution is then cooled and packed in ice and the arsenic, which is almost invariably present, is removed by passing through H_2S for several hours. The As_2S_3 is filtered off in a weighed Gooch crucible, washed first with CS_2 and alcohol then with concentrated hydrochloric acid and dried at 100°, and weighed as As_2S_3.

Antimony. The filtrate from above is put into 250 cc. volumetric flask, rinsing the beaker well with concentrated hydrochloric acid and an equal part of water. All

the H_2S is removed by passing through a current of air. Five grams of tartaric acid are added and the liquid diluted to the mark.

Twenty-five cc. of the solution are measured out with a pipette and are neutralized with dry sodium bi-carbonate—keeping covered to avoid loss—finally a pinch of sodium bi-carbonate and a cubic centimeter of clear starch solution is added and the mixture is titrated with N/10 iodine solution.

<div align="center">1 cc. N/10 Iodine = 0.0060 grams Sb</div>

The Analysis of Oxide of Cobalt

Arsenic. One gram finely pulverized sample is fused at low heat with ten grams bisulfate of potassium for three hours. The melt is extracted with water acidified with sulfuric acid and the arsenic is precipitated from the warm acid solution with H_2S, collected in a weighed Gooch crucible, washed with water containing H_2S and dried at 100° for one hour and weighed as As_2S_3.

Cobalt. The filtrate from above is boiled, and at the same time air is drawn through to remove the H_2S, and it is then treated by Fisher's Potassium Nitrite method[1] to separate the cobalt and the nickel.

The concentrated solution containing salts of both metals is treated with pure potassium hydroxide to alkaline reaction, made slightly acid with acetic acid, and to this a concentrated solution of pure potassium nitrite that has been made slightly acid with acetic acid is added. After vigorous stirring, the mixture is allowed to stand twenty-four hours in a warm place. Before filtering, a little of the clear solution is pipetted off and treated with more potassium nitrite to see if the precipitation of the cobalt has been complete. If a precipitate is formed, the whole solution is treated with more potassium nitrite and again allowed to stand until complete precipitation is ef-

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[1] Treadwell, Vol. II, p. 130.

fected. The precipitate is then filtered and washed with a barely acid 5 per cent solution of potassium nitrite until 1 cc. of the filtrate, after being boiled with hydrochloric acid and treated with caustic potash and bromine water, no longer gives a black precipitate of nickelic hydroxide. The cobalt precipitate is then transferred to a porcelain dish, covered, and hydrochloric acid is gradually added until there is no further evolution of nitric oxide, and after filtering, the cobalt is precipitated by means of caustic potash and bromine water.

The precipitate is filtered off, using blue ribbon filter paper, dried, and ignited. After cooling it is treated with water in order to remove the small amount of alkali which is always present, after which the residue is ignited in a stream of hydrogen and weighed as metal. After weighing, the metal is dissolved in hydrochloric acid, evaporated to dryness, the dry mass moistened with hydrochloric acid, then treated with water, and the small residue of silicic acid is filtered off. This residue is ignited and its weight subtracted from that obtained after the ignition in hydrogen.

Nickel. The filtrate containing the nickel is treated with hydrochloric acid until the nitrite is completely decomposed, and the nickel is precipitated with potassium hydroxide and bromine water as brownish-black nickelic hydroxide [Ni $(OH)_3$.]

The precipitate—which seldom contains more than ten milligrams of nickel—is washed with hot water, collected on a filter and is dried, ignited separately from the filter, and weighed as NiO, in which form it was probably present in the oxide.

Steel Plate

The steel best adapted for enameled ware is of very low carbon value and extremely low in the other impurities, in fact, the nearer pure iron the better. Of the steel

plate used by the Columbian Enameling and Stamping Company, the best satisfaction was obtained from those giving the following analysis:

Sulfur from .040% to .050%; phosphorous from .030% to .090%; silica less than .01%; manganese from .060% to .040%, and carbon less than 0.10%. The sheets must be of an even gauge for seamless drawn work and of a dark soft quality, which allows them to be drawn without tearing. When the vessel is made without drawing and sheets are used flat, this evenness of gauge is not so much an object. The grain in all cases must be as open as possible. The sheet must be low in carbon and sulfur, as these develop gases at temperatures of the muffle, which would cause the enamel to peel off.

Samples of the steel plate are obtained from drillings taken from eight or ten sheets stacked in a pile, and drilled holes are run every two inches on the diagonal of the plate. Drillings are sampled down to twenty-five grams, which are kept in stoppered bottles. The method of analysis is that commonly employed by steel-works chemists, and can easily be found in print elsewhere, and for that reason will not be given here.

ATOMIC AND MOLECULAR WEIGHTS AND FACTORS USED IN CERAMIC CALCULATIONS[1]

Aluminum,

oxide,	Al_2O_3	*102.2	†R_2O_3 — 102
hydrate,	$Al_2O_3.3H_2O$	156.3	R_2O_3 — 156

$$
\begin{aligned}
1\ Al\text{—oxide} &= 1.529\ \text{Al—hydrate} \\
" &= 6.536\ \text{Al—sulfate} \\
" &= 8.893\ \text{Ammonia Alum} \\
" &= 2.534\ \text{China Clay} \\
" &= 2.548\ \text{Cryolite} \\
" &= 9.305\ \text{Potash Alum} \\
" &= 5.154\ \text{Soda Feldspar} \\
" &= 3.069\ \text{Am. Enamel Clay}
\end{aligned}
$$

Antimony,

oxide,	Sb_2O_3	288.4	R_2O_3 — 288
tetroxide,	Sb_2O_4	304.4	R_2O_3 — 304
pentoxide,	Sb_2O_5	320.4	R_2O_3 — 320
sulfide,	Sb_2S_3	336.6	R_2O_3 — 337

$$
\begin{aligned}
1\ Sb\text{—trioxide} &= 1.167\ \text{Sb—trisulfide} \\
" &= 1.111\ \text{Sb—pentoxide}
\end{aligned}
$$

Arsenic, trioxide, As_2O_3 197.9 R_2O_3 — 198

Barium,

carbonate,	$BaCO_3$	197.4	RO — 197
sulfate,	$BaSO_4$	233.4	RO — 233

$$
\begin{aligned}
1\ Ba\text{—carb.} &= 0.777\ \text{Ba—oxide} \\
1\ Ba\text{—oxide} &= 1.287\ \text{Ba—carb.} \\
1\ Ba\text{—sulfate} &= 0.657\ \text{Ba—oxide}
\end{aligned}
$$

Boric Acid, $B_2O_3.3H_2O$ 124.0 B_2O_3 — 124

   (Fused), B_2O_3 70.0 B_2O_3 — 70

Borax, $Na_2B_4O_7.10H_2O$ 382.2 $RO.2B_2O_3$ — 382

   (Fused), $Na_2B_4O_7$ 202.0 $RO.2B_2O_3$ — 202

$$
\begin{aligned}
1\ \text{Boric Acid} &= 0.548\ B_2O_3 \\
1\ B_2O_3 &= 1.771\ \text{Boric Acid} \\
1\ \text{Borax} &= 0.529\ \text{Borax Fused} \\
1\ \text{Borax} &= 0.162\ \text{Na—oxide} \\
1\ \text{Borax} &= 0.366\ B_2O_3 \\
1\ \text{Borax (Fused)} &= 0.307\ \text{Na—oxide} \\
1\ \text{Borax} \quad " &= 0.693\ B_2O_3 \\
1\ \text{Borax} \quad " &= 1.892\ \text{Borax}
\end{aligned}
$$

[1]Compiled by Robert D. Landrum, mainly from Report of Committee of Equivalent Weights, Transactions of American Ceramic Society, Vol. II, pages 196 to 278. The reader is referred to this report for full explanation and method of using these equivalent weights.

*Molecular Weight. †Equivalent Weight.

Cadmium sulfide, CdS *144.5 †CdS — 145

Calcium,

carbonate,	$CaCO_3$	100.1	RO	— 100
fluoride,	CaF_2	78.1	RO	— 78
oxide,	CaO	56.1	RO	— 56
phosphate,	$Ca_3(PO_4)_2$	310.3	RO	— 103
sulphate,	$CaSO_4.2H_2O$	172.2	RO	— 172

1 Ca—fluoride   = 0.718 Ca—oxide
       "   = 0.487 F.
1 Ca—oxide   = 1.786 Ca—carbonate
       "   = 1.321 Ca—hydrate
       "   = 3.073 Ca—sulfate (Gypsum)
1 Ca—phosphate = 0.542 Ca—oxide

China Clay, $Al_2O_32SiO_2$
                $2H_2O$ 258.0 $\left.\begin{array}{l}R_2O_3 \\ 2SiO_2\end{array}\right\}$ — 258

Cerium

dioxide,	CeO_2	172.3	CeO_2	— 172
sesquioxide,	Ce_2O_3	328.3	R_2O_3	— 328

Chromate of Barium, $BaCrO_4$ 253.5 $\left.\begin{array}{l}2RO \\ R_2O_3\end{array}\right\}$ — 506

Chromate of Lead, $PbCrO_4$ 323.1 $\left.\begin{array}{l}2RO \\ R_2O_3\end{array}\right\}$ — 646

Chromium Oxide, Cr_2O_3 152.0 $\left.\begin{array}{l}2RO \\ R_2O_3\end{array}\right\}$ — 152

1 Cr—oxide   = 1.658 Am—bichromate
       "   = 2.001 Am—chromate
       "   = 1.828 Cr—hydrate
       "   = 5.261 Cr—nitrate
       "   = 4.710 Cr—sulfate
       "   = 6.288 Cr—ammonia alum

Cobalt

carbonate,	$CoCO_3$	119.0	RO	— 119
chloride,	$CoCl_2.6H_2O$	238.0	RO	— 238
nitrate,	$Co(NO_3)_2.6H_2O$	291.1	RO	— 291
oxide,	Co_2O_3	166.0	RO	— 83
oxide,	CoO	75.0	RO	— 75
oxide (blk.),	Co_3O_4	241.0	RO	— 80
sulphate,	$CoSO_4.7H_2O$	281.2	RO	— 281

1 Co—carbonate = 0.630 Co—ous oxide
1 Co—chloride   = 0.315 Co—ous oxide
1 Co—nitrate   = 0.258 Co—ous oxide
1 Co—ic oxide   = 0.904 Co—ous oxide
1 Co—ous oxide = 1.587 Co—carbonate
       "   = 3.173 Co—chloride
       "   = 1.173 Co—ic oxide
       "   = 3.749 Co—sulfate

*Molecular Weight. †Equivalent Weight.

Copper

oxide (red)	Cu_2O	*143.1	†RO —	72
oxide (black)	CuO	79.6	RO —	80
sulphate,	$CuSO_4.5H_2O$	249.7	RO —	250

1 Cu—oxide (Blk.) = 0.899 Cu—oxide (Red)
1 Cu—oxide (Blk.) = 3.137 Cu—sulfate
1 Cu—oxide (Red) = 1.112 Cu—oxide (Blk.)
1 Cu—sulfate = 0.319 Cu—oxide (Blk.)

Cornwall Stone, $1RO.2.5\ Al_2O_3$

$20.SiO_2$ $\quad$ 1550.0 $\left.\begin{array}{l} 1\,RO \\ 2.5\ R_2O_3 \\ 20.0\ SiO_2 \end{array}\right\}1550$

Cryolite $\quad Na_7AlF_6 \quad$ 210.0 $\left.\begin{array}{l} 3RO \\ Al_2O_3 \end{array}\right\}$ — 420

Feldspar (Soda) $\quad \begin{array}{l} Na_2O.Al_2O_3 \\ 6SiO_2 \end{array}$ $\quad$ 524.0 $\left.\begin{array}{l} 1RO \\ 1R_2O_3 \\ 6SiO_2 \end{array}\right\}$ — 524

Feldspar (Lime-Soda) $\begin{array}{l} CaO) \\ Na_2O) \end{array} \begin{array}{l} Al_2O_3 \\ 5SiO_2 \end{array}$ $\quad$ 520.0 $\left.\begin{array}{l} 1RO \\ 1R_2O_3 \\ 5SiO_2 \end{array}\right\}$ — 520

Feldspar (Potash) $\quad \begin{array}{l} K_2O.Al_2O_3 \\ 6SiO_2 \end{array}$ $\quad$ 557.0 $\left.\begin{array}{l} 1RO \\ 1R_2O_3 \\ 6SiO_2 \end{array}\right\}$ — 557

Ferric Oxide $\quad Fe_2O_3 \quad$ 159.7 $\quad R_2O_3$ — 160

Ferrous Sulphide $\quad FeS \quad$ 87.9 $\quad R_2O_3$ — 176

Ferric Oxide

$\quad$ (Magnetic) $\quad Fe_3O_4 \quad$ 231.5 $\quad R_2O_3$ — 155

Ferrous Sulphate $\quad FeSO_4.7H_2O \quad$ 278.0 $\quad R_2O_3$ — 556

Lead Acetate $\quad \begin{array}{l} Pb(C_2H_3O_2)_2 \\ 3H_2O \end{array}$ $\quad$ 379.2 $\quad$ RO — 379

$\quad$ carbonate (basic) $\ 2(PbCO_3)$

$\quad\quad\quad\quad Pb(OH)_2 \quad$ 775.3 $\quad$ RO — 258

$\quad$ oxide (red) $\quad Pb_3O_4 \quad$ 685.3 $\quad$ RO — 228

Litharge $\quad PbO \quad$ 223.1 $\quad$ RO — 222

Magnesium

carbonate	$MgCO_3$	84.3	RO —	84
oxide	MgO	40.3	RO —	40

1 Mg—carbonate = 0.479 Mg—oxide
1 Mg—oxide = 2.089 Mg—carbonate

*Molecular Weight. †Equivalent Weight.

Manganese

carbonate	$MnCO_3$	*114.9	†RO	— 115
di-oxide	MnO_2	86.9	RO	— 87

Nickelic Oxide $\quad$ NiO $\qquad$ 74.7 $\quad$ RO $\quad$ — 75

Nickelous Oxide $\quad$ Ni_2O_3 $\qquad$ 165.4 $\quad$ RO $\quad$ — 83

Nickel Sulfate $\quad$ $NiSO_4 . 7H_2O$ $\quad$ 280.9 $\quad$ RO $\quad$ — 281

$$1 \; Ni_2O_3 \;\;\; = \; 0.903 \; NiO$$
$$1 \; NiO \;\;\; = \; 1.107 \; Ni_2O_3$$
$$1 \; NiO \;\;\; = \; 3.760 \; Ni\text{—sulfate}$$

Potash Alum $\qquad$ $K_2SO_4Al_2(SO_4)_3$

$\qquad\qquad\qquad$ RO
$\qquad$ $24H_2O$ $\qquad$ 949.1 $\;$ Al_2O_3 — 949

Potassium

antimonate			RO	
	$KSbO_3$	207.3	Sb_2O_5	— 414
bichromate	$K_2Cr_2O_7$	294.2	RO ⎰—	
			$2R_2O_3$⎱	— 294
carbonate	$K_2CO_3 . 2H_2O$	174.2	RO	— 174
carbonate (calcined)	K_2CO_3	138.2	RO	— 138
nitrate	KNO_3	101.1	RO	— 202

$$1 \; K\text{—nitrate} \;\; = \; 0.466 \; K\text{—oxide}$$
$$\text{"} \;\; = \; 0.683 \; K\text{—carbonate}$$
$$\text{"} \;\; = \; 0.737 \; K\text{—chloride}$$
$$\text{"} \;\; = \; 0.863 \; K\text{—sulfate}$$
$$1 \; K\text{—oxide} \;\; = \; 1.467 \; K\text{—carbonate (anhydrous)}$$
$$\text{"} \;\; = \; 1.848 \; K\text{—carbonate (crystal)}$$
$$\text{"} \;\; = \; 1.582 \; K\text{—chloride}$$
$$\text{"} \;\; = \; 1.192 \; K\text{—hydrate}$$
$$\text{"} \;\; = \; 2.145 \; K\text{—nitrate}$$
$$\text{"} \;\; = \; 1.849 \; K\text{—sulfate}$$
$$\text{"} \;\; = \; 5.927 \; K\text{—feldspar}$$
$$\text{"} \;\; = \; 10.066 \; K\text{—alum}$$

Selenium	Se	79.2	SeO_2 —	79
Oxide	SeO_2	111.2	SeO_2 —	111
Silica	SiO_2	60.3	SiO_2 —	60

*Molecular Weight. †Equivalent Weight.

Sodium

antimonate	$NaSbO_3$	*191.2	†$ROSb_2O_5$	— 382
carb. (cryst.)	$Na_2CO_3 . 10H_2O$	286.2	RO	— 286
carb. (soda ash)	Na_2CO_3	106.0	RO	— 106
chloride	$NaCl$	58.5	RO	— 117
hydrate	$NaOH$	40.0	RO	— 80
nitrate	$NaNO_3$	85.0	RO	— 170
silico fluoride	Na_2SiF_6	188.3	$ROSiF_6$	— 189

1 Na—carbonate (crystals) $= 0.371$ Na—carbonate (anhydrous)

1 Na—carbonate (crystals) $= 0.216$ Na_2O

1 Na—carbonate (anhydrous) $= \begin{matrix} 2.698 \text{ Na—carbonate (crystal)} \\ 0.585 \text{ } Na_2O \end{matrix}$

1 Na—carbonate (anhydrous) $= \begin{matrix} 0.531 \text{ } Na_2O \\ 0.774 \text{ } Na_2O \end{matrix}$

1 Na—chloride $= 0.365$ Na_2O
1 Na—hydrate $= 6.161$ Borax (crystal)
1 Na—nitrate $= 3.258$ Borax (anhydrous)
1 Na_2O $= 4.613$ Na—carbonate (crystal)
" $= 1.710$ Na—carbonate (anhydrous)
" $= 1.887$ Na—chloride
" $= 1.290$ Na—hydrate
" $= 2.742$ Na—nitrate
" $= 5.193$ Na—sulfate (crystal)
" $= 2.290$ Na—sulfate (anhydrous)
" $= 8.500$ Na—feldspar
" $=$
" $=$

Strontium

carbonate	$SrCO_3$	147.6	RO	— 148
sulfate	$SrSO_4$	183.7	RO	— 184

Tin

chloride	$SnCl_2 . 2H_2O$	226.0	RO	— 226
oxide	SnO_2	151.0	RO	— 151

Titanium Oxide TiO_2 80.0 TiO_2— 80

Uranium

oxide	UO_2	270.5	R_2O_3— 543	
oxide (com'l)	$Na_2O . U_2 . O_6$			
	$6H_2O$	746.0	$\left. \begin{matrix} RO \\ R_2O_3 \end{matrix} \right\}$— 746	

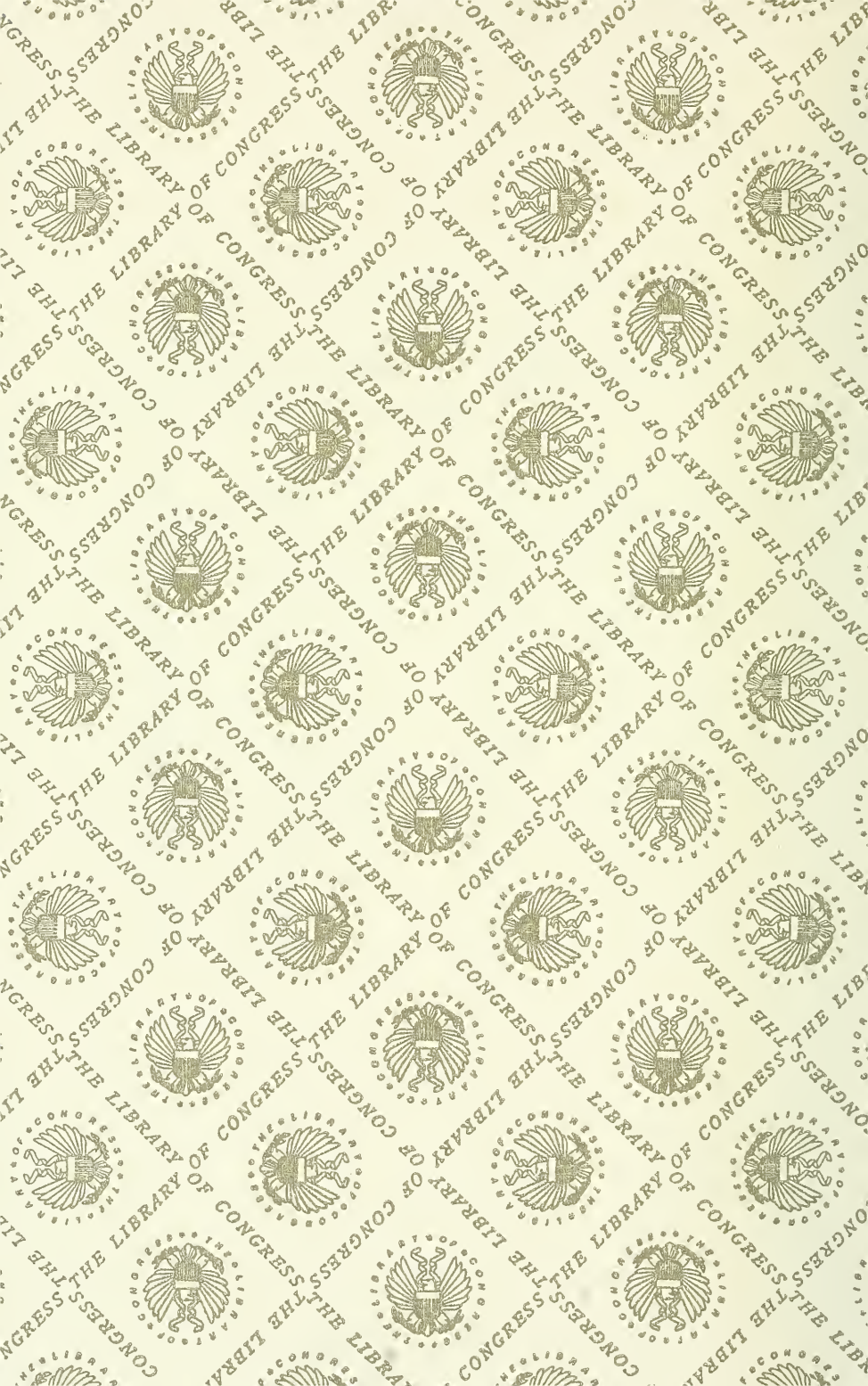**Zirconium Oxide** ZrO_2 122.6 ZrO_2 — 123

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*Molecular Weight. †Equivalent Weight.

CUBICAL COEFFICIENT OF EXPANSION

in Millimeters per degree Centigrade, as determined by Winkelmann and Schott and Mayer and Havas
(See Sprechsaal 1911, No. 13)

AlF_3	$= 4.4 \times 10^{-7}$	MgO	$= 0.1 \times 10^{-7}$
Al_2O_3	$= 5.0 \times 10^{-7}$	MnO	$= 0.1 \times 10^{-7}$
As_2O_5	$= 2.0 \times 10^{-7}$	Na_3AlF_6	$= 7.4 \times 10^{-7}$
BaO	$= 3.0 \times 10^{-7}$	NaF	$= 7.4 \times 10^{-7}$
BeO	$= 4.7 \times 10^{-7}$	Na_2O	$= 10.0 \times 10^{-7}$
B_2O_3	$= 0.1 \times 10^{-7}$	NiO	$= 4.0 \times 10^{-7}$
CaF_2	$= 2.5 \times 10^{-7}$	PbO	$= 4.2 \times 10^{-7}$
CaO	$= 5.0 \times 10^{-7}$	P_2O_5	$= 2.0 \times 10^{-7}$
CeO_2	$= 4.2 \times 10^{-7}$	Sb_2O_5	$= 3.6 \times 10^{-7}$
CoO	$= 4.4 \times 10^{-7}$	SiO_2	$= 0.8 \times 10^{-7}$
Cr_2O_3	$= 5.1 \times 10^{-7}$	SnO_2	$= 2.0 \times 10^{-7}$
CuO	$= 2.2 \times 10^{-7}$	ThO_2	$= 6.3 \times 10^{-7}$
Fe_2O_3	$= 4.0 \times 10^{-7}$	TiO_2	$= 4.1 \times 10^{-7}$
K_2O	$= 8.5 \times 10^{-7}$	ZrO_2	$= 2.1 \times 10^{-7}$
LiO_2	$= 2.0 \times 10^{-7}$	ZnO	$= 1.8 \times 10^{-7}$

237 90